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Composites Based on Post-Industrial Wood Plastic Waste and Ultrasonic Treated Muscovite

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In this work muscovite was ultrasonically treated to obtain composites with post-industrial wood plastic residues. The muscovite was ultrasonicated for 30 or 60 min and mixed with the polymeric matrix at a constant level of 15% (weight percentage). The composites were prepared in a single-screw extruder and formed into flat films for characterization. SEM images of the ultrasonicated muscovite revealed the occurrence of delamination, while the particle size distribution results suggested a decrease in size with longer sonication time. FTIR spectra also indicated the occurrence of delamination of the material. The composites exhibited a slight increase in density and a large increase in impact resistance of the samples with ultrasonicated muscovite. The XRD of the composites suggested the occurrence of alignment of the mineral in the matrix. The results indicate that ultrasonication is an effective method to improve the interaction and dispersion of muscovite with wood plastic waste to obtain composites.

Keywords*: Polymeric composites, wood plastic, muscovite, ultrasound treatment.*

1. Introduction

Since their advent, composite materials have attracted investigation by researchers from different areas due to the wide variety of properties and potential uses of these materials in areas such as aerospace, automotive, civil construction, sports, biomedical devices and others[1].

The current development of composites aims to meet the growing global concern over implementing sustainable practices throughout the material production process. In this sense, there has been a great effort to find viable composite systems that use, for example, matrices based on post-consumer, post-industrial or recycled polymers, along with and natural inorganic particles as fillers, such as minerals[2,3,4].

A sustainable practice in accordance with this scenario is the use of wood plastic as polymeric matrix and aluminosilicate minerals with a lamellar structure, such as micas (muscovite, biotite, phlogopite, etc.), as inorganic fillers[5,6].

Wood plastic is usually manufactured from the recycling of various types of plastics, which are reprocessed and pigmented to generate new products. This material has applications similar to those of common wood, so it can be nailed, screwed, riveted or glued. However, because it is manufactured primarily from polyolefins, its thermal and mechanical resistance is not ideal, and warping and discoloration during use are common, mainly due to exposure to the sun's heat and other inclement weather conditions[4,7].

An alternative to improve the properties of wood plastic is the incorporation of clay minerals as reinforcing fillers. Brazil has large reserves of several minerals, such as muscovite ($KAl_2[Si_3AlO_{10}](OH,F_2)$), which is a subtype of mica which can be found in abundance in the Northeast region. However, mining of clay minerals in this region is mainly artisanal, which typically is carried out without precautions against environmental pollution and also means the clay has low added value. On the other hand, these minerals' natural origin means they can be processed without use of potentially polluting chemicals[4,7].

Almeida et al.[7] studied the influence of muscovite content (0 – 20%) on wood plastic properties. An improvement in properties was observed, mainly hardness, density and melt flow index (MFI), with mica content up to 15%, but low efficiency of mineral dispersion and its interaction with the matrix was observed, suggesting the need to use compatibilizing agents.

Gerardo et al.[4] investigated the addition of muscovite with constant proportion of 15% and varied particle size (less than 125, 106, 75 and 45μm). They found that the size of the particles did not significantly influence the chemical and mechanical properties studied. This was considered an advantage, since obtaining smaller particles requires greater energy consumption. The authors also mentioned the need to use some alternatives to improve the dispersion and interaction of the mineral with the matrix.

An alternative to improve the adhesion between polymers and clay minerals is to increase the number of mineral lamellae, on which compensating cations (such as K+) can be found that promote more effective interactions between matrix and filler. The literature suggests the use of ultrasound treatment for delamination of minerals with a lamellar structure, such as micas[8,9].

Ultrasound is an eco-friendly method, since it requires little or no use of chemicals that are toxic to humans and/or

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the environment. Ultrasound promotes cavitational collapse of bubbles on solid surfaces, leading to microjets and shock-wave impacts on the surface of solids, along with interparticle collisions, which can result in smaller particle size and delamination of the mineral[10,11,12].

Several studies have been published[8,9,10,11,12] on the use of sonication for treatment of different minerals. However, research aimed at treating minerals to obtain composites is scarce.

Takei et al.[9] described the use of sonication to obtain composites. The effect of ultrasonic treatment of sepiolite clay on the dispersion and tensile strength of composites of sepiolite and NBR rubber was evaluated. An increase in tensile strength from 3 to 8 MPa was observed for the composites using low frequency ultrasonication (28 kHz).

In this context, in the present study we applied ultrasound treatment of muscovite, which was used in the preparation of composites with post-industrial residues of wood plastic (WP), maintaining the proportion of muscovite at 15% and particle size less than 125 μm.

2. Experimental Procedures

2.1. Materials

The muscovite used in this work is from region of Borborema-Seridó (states of Rio Grande do Norte and Paraíba in Brazil) and was collected by the Mineral Technology Center (CETEM). In the cited regions, the mining of this muscovite is carried out for local people as a subsistence activity, so the mineral obtained has low added value.

This muscovite was treated according to the method developed at the CETEM. The mineral was milled with industrial knives until granulometry of less than 2 mm. The resulting product was separated from impurities by table gravity concentration, where the impurities are removed by density difference while the material slides on a vibrating table. Then the purified product was ground in a laboratory knife mill and dry sieved to obtain material with granulometric classification smaller than 125 μm[10].

The wood plastic waste used was provided by Companhia Municipal de Limpeza Urbana (Comlurb, the municipal sanitation agency in the city of Rio de Janeiro). According to data obtained from previous works, this material is composed mainly of high-density polyethylene (HDPE), other polymers in smaller quantities (i.e., PE, EVA) and additives[4,7]. The process to prepare the material for use in the composite initially consisted of manual separation to eliminate undesirable coarse residues, followed by manual cutting into smaller sizes to allow insertion into the feeder of the single screw extruder[7].

The use of muscovite with low added value and wood plastic waste reinforces the sustainable character of this study, since the development of research using these materials contributes to reduce the environmental impact caused by them.

2.2. Ultrasonic treatment

Dispersions (5 wt.%) of muscovite samples in distilled water were exposed to ultrasound for 30 or 60 min using an Ultraclean 1600 device. A power supply of 40 kHz and 500 W was used. The treatment temperature varied between 30 and 40 °C during the process. The samples were dried at 60 °C for 24 h.

Ultrasound has been referred to as an eco-friendly method, since it requires little or no use of chemicals that are toxic to humans and/or the environment.

2.3. Composites preparation

The particle size of muscovite (less than 125 μm) and proportion in the WP/mica composites (85/15% by weight) were kept constant. Muscovite (mica) ultrasonically treated for 30 (WP/Mica125US30), 60 min (WP/Mica125US60) and without treatment (WP/Mica125) was used to prepare the composites. A sample composed of wood plastic waste only (WP) was also prepared. The samples was fed into a single-screw extruder (AX Plastics 1626) equipped with three temperature zones (190, 200 and 220 ºC from the feed to die), rotating at 66 rpm. Then the samples were ground in a knife mill (less than 2 mm), and to obtain samples in film format the materials were pressed at 6 tons at 220 ºC for 5 min and cooled in a cold press for 5 min. Figure 1 shows a sketch of the experimental setup for composite preparation.

2.4. Characterization

2.4.1. Particle size measurement

The muscovite particle size distribution was determined by the laser diffraction technique using a Malvern Mastersizer 2000 analyzer. The measurements were carried out in distilled water. The nominal diameters D (0.1), D (0.5) and D (0.9) were calculated by averaging the mean values of each measurement.

2.4.2. Density, Hardness and melt index flow (MFI)

The WP samples and composites were characterized according to density, hardness and melt flow index MFI. For the density tests, the ASTM D792 (2020)[13] Standard was used. A Gehaka model DSL 910 densimeter and five specimens of each composite were used. The Shore D hardness test was performed on composite materials in accordance with the ASTM D2240 (2021)[14] Standard, using a Shore D hardness tester (Type GS 702), at five different points of each specimen. To determine the melt flow index (MFI), a fluidity index measuring device (CEAST-Quick Index) was used in accordance with the ASTM D1238-13 (2013)[15] Standard, at a temperature of 190 ºC and load of 2.16Kg. Five specimens of each sample were analyzed.

2.4.3. FTIR analysis

Fourier-transform infrared spectra were acquired using a Nicolet 6700 FTIR spectrometer (Thermo Scientific). The samples were mounted on an attenuated total reflectance (ATR) accessory equipped with a ZnSe crystal prior to scanning. The spectra were obtained with accumulation of 120 scans and resolution of 4.182 cm^{-1} in the 500 - 4000 cm^{-1}.

2.4.4. Impact resistance

The IZOD impact tests were carried out in accordance with ASTM D256-10 (2018)[16] with an impact pendulum

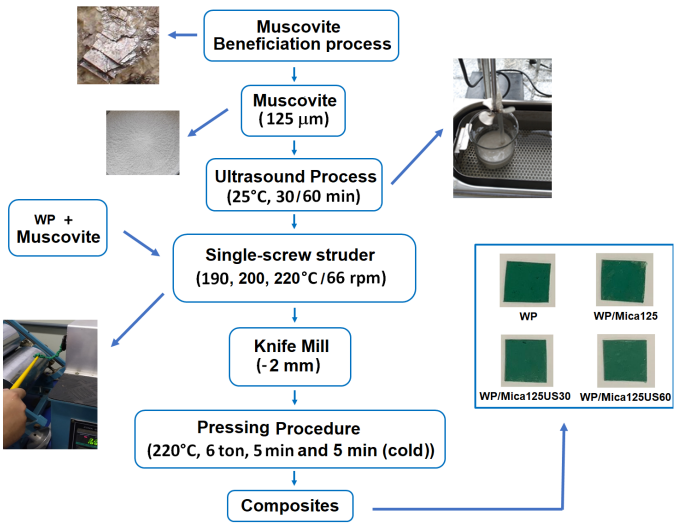

Figure 1. Sketch of the experimental set-up for composites preparation.

machine (Ceast model 9050), with a 2.7J impact hammer. Five test specimens of each composition were analyzed.

2.4.5. Morphology by SEM

After the impact tests, the fracture surface morphology of the samples was analyzed by scanning electron microscopy (SEM) using a Hitachi TM3030Plus microscope. The samples were covered with a thin layer of gold.

2.4.6. X-ray diffraction (XRD)

The XRD analysis was performed with a Bruker-AXS D8 Advance Eco diffractometer, using Cu kα radiation (λ= 1.54180 Å, 40 kV/25 mA) and 2θ angle range from 4° to 70°.

3. Results and Discussion

3.1. Muscovite samples characterization

Table 1 shows the results of average particle size of muscovite samples before and after ultrasound treatment. The D(0.1), D(0.5) and D(0.9) values represent the particle sizes below which 10, 50 and 90% of the sample falls, respectively. There was gradual size reduction of the mineral particle size with increasing sonication time. The samples processed for 90 min and 120 min were not used to prepare composites, but this result is included here to demonstrate the tendency caused by the ultrasound treatment[8,10,17]. The data obtained also revealed the presence of fine particles (-20 µm). Similar results have been reported by other authors[4,10,17] and are related to the grinding method (knife mills) and screening of the mineral. Also, according to Lapčík et al.[5] and Gerardo et al.[4], this particle size distribution is desirable for composites because fine particles are better able to fill the voids in the matrix.

The SEM images of untreated muscovite and sonicated muscovite samples, as shown in Figure 2a-2f, indicated the occurrence of delamination accompanied by decreasing particle thickness with increasing ultrasound treatment time. Figure 2e depicts the delamination process of some muscovite particles. The delamination process of clay minerals, such as muscovite, increased the number of mineral lamellae on which compensating cations (such as K+) can be found that promote more effective interactions (dipole-dipole and ion-dipole) between matrix and filler[8,9].

Table 1. Particle size diameters of muscovite (mica) samples before and after ultrasound treatment.

Samples	Particle size (µm)		
	D (0.1)	D (0.5)	D (0.9)
Mica125	19.96	104.44	212.77
Mica125US30	20.94	104.01	207.65
Mica125US60	21.00	105.83	209.51
Mica125US90	21.95	99.48	203.82
Mica125US120	17.80	65.03	143.45

Figure 2a, 2c, 2e also show the usual random planar shape of the muscovite mineral and the presence of different particle sizes, in agreement with the particle size distribution analysis[4,8,17].

The FTIR-ATR results are shown in Figure 3. The spectra of untreated and sonicated muscovite samples exhibited the vibrations as expected for mica mineral. The OH stretching vibrations, occurred between the 3750-3550 cm^{-1} region. The vibrations of the mica group minerals can be observed in the 1200-700 cm^{-1} region (Si-O stretching) as pointed by Ismail et al.[18], Almeida et al.[7] and Gerardo et al.[4]. Vibrations of the interlayer cations usually are located in the range of 400-50 cm^{-1}, so it is not possible to see them in our spectra.

The spectra for the sonicated muscovite samples showed a decrease in the absorption of the bonds between 1200-500 cm^{-1}, attributed to the process of breaking the interatomic bonds (i.e., Al-O, Si- O), due to the mineral delamination process, as also reported by Brown and Liu[19]. We also observed the appearance of low intensity absorption bands in the region of 2500-1200 cm^{-1}. Since muscovite is a mineral of natural origin, it is common for other minerals (e.g., quartz, hematite, feldspars) to be incorporated in the mineral structure. Despite the processing and removal of

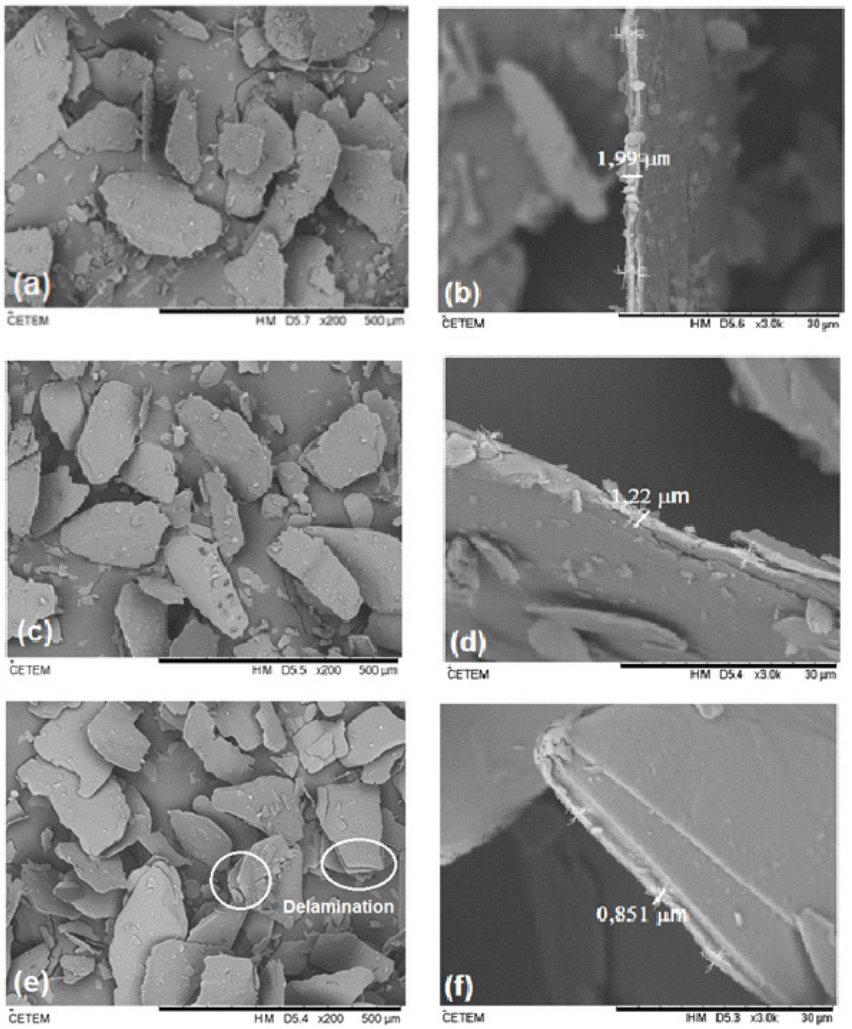

Figure 2. SEM micrographs of: (a) Mica125, (b) Thickness of Mica125, (c) Mica125US30, (d) Thickness of Mica125US30, (e) Mica125US60 and (f) Thickness of Mica125US60.

most impurities, a small amount was trapped in the lamellae and released during the delamination process[10].

X-ray diffraction analysis of muscovite before and after ultrasound treatment showed the same profile of the three samples, as reported by other authors[8,18] who also stated that ultrasonic treatment for short periods does not usually cause structural alteration in minerals. Figure 4 illustrates the XRD pattern for the mica125US30 sample, which exhibits the typical profile of muscovite[18].

3.2. Composites characterization

The results of density, Shore D hardness, MFI and IZOD impact tests are summarized in Table 2. The density value of the WP sample was in accordance with literature data indicating values between 0.7 and 0.8 g/cm^3 for this material[4,7]. The composites' density increased slightly with muscovite addition, which can be attributed to a decrease in free volume as a consequence of good matrix/filler adhesion[5]. No significant changes in density were observed for the sonicated samples.

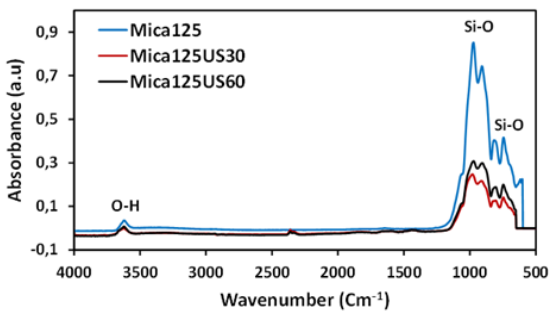

Figure 3. FTIR-ATR of muscovite samples before and after ultrasound treatment.

The hardness was similar for all the samples. This result was expected because, according to data from the literature[20,21] this property tends to increase with an increase in filler content or by chemical alterations of the minerals. However, MFI analysis showed an increase in viscosity

with muscovite addition. The corresponding decrease in the melt flow index is usually related to restriction of the movement of the polymer chains induced by the mineral filler, which also suggests good interaction between the phases[3,5].

The results of the impact test showed both improvement of the composites over the pure sample and improvement with increasing ultrasonication time. The sample WP/Mica125US60, which was treated for 60 min, showed an increase of about 77% (related to the mean value of the measurements, without considering the standard deviations) in relation to the WP sample, similar to the findings of Melo et al.[3] and Bharathiraja et al.[22], Further according to these authors, agglomerated particles tend to worsen the impact performance of the material, so this result suggests an improvement in dispersion with the use of ultrasonic treatment.

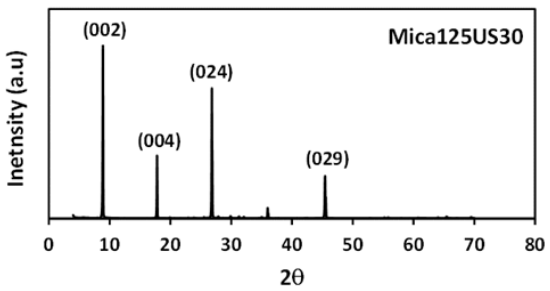

Figure 4. XRD pattern of the Mica125US30 sample.

Figure 5 shows SEM micrographs of the fractured surfaces of the samples after the impact tests. It was possible to observe that the sample without sonication (WP/Mica125, Figure 5b) had regions with greater mica concentration and others with low concentration, while in the composites with ultrasonicated mineral the distribution was more homogeneous, as illustrated in Figure 5c for the WP/Mica125US30 sample. There also were regions showing the typical ductile fracture profile, such as for WP/Mica125US60 in Figure 5d, in accordance with the impact test result. We also observed that only a small quantity of muscovite ejections on the fracture surface occurred, indicating along with the other results good mineral/polymer adhesion[4,5,7].

Figure 6 presents the XRD patterns of WP, muscovite and composite samples. The curve for the wood plastic sample, Figure 6e, shows peaks of different types of

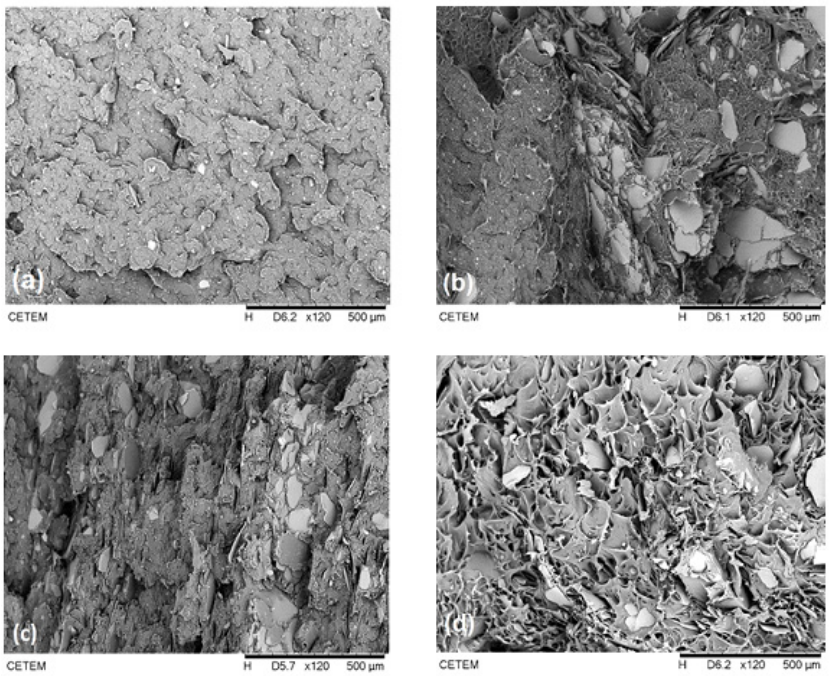

Figure 5. SEM micrographs of the fractured surfaces of the samples of impact tests: (a) WP, (b) WP/Mica125, (c) WP/Mica125US30 and (d) WP/Mica125US60.

Table 2. Density, Hardness D, MFI and IZOD impact results for the composites.

Samples	Density (g/cm^3)	Hardness (Shore D)	MFI (g/10min)	Impact (kJ/m^2)
WP	0.807 ± 0.032	61.67 ± 1.53	1.228 ± 0.062	10.09 ± 1.40
WP/Mica125	1.211 ± 0.020	60.00 ± 0.00	0.208 ± 0.019	13.87 ± 6.61
WP/Mica125US30	1.112 ± 0.030	60.67 ± 1.15	0.132 ± 0.034	16.63 ± 4.52
WP/Mica125US60	1.123 ± 0.032	60.33 ± 1.15	0.270 ± 0.020	17.92 ± 4.80

polymers due to the mixing of several polymeric residues. The diffractograms of all composites exhibited very similar profiles (Figure 6b, 6c and 6d), showing that muscovite did not alter the original semi-crystalline structure of the polymeric matrix. However, the interaction of the mineral with the polymer promoted some alignment of the mineral particles that favored certain muscovite diffraction angles (28°, 37°, 47° and 66°) in comparison with the profile of pure muscovite, in Figure 6a[23]. This alignment of the mineral can be seen in Figure 5c. Furthermore, the ultrasonic treatment did not modify the structure of the mineral, as reported by other authors regarding sonication for short periods[8,9].

Figure 7 exhibits the FTIR spectra of the samples. The WP peaks in the 2950 and 2850 cm^{-1} region correspond to C-H stretching vibrations; peaks in the 1450-1350 cm^{-1} region correspond to CH_2 bending vibrations; and peaks in the region of 730 to 717 cm^{-1} refer to CH_2 rocking vibrations[24,25].

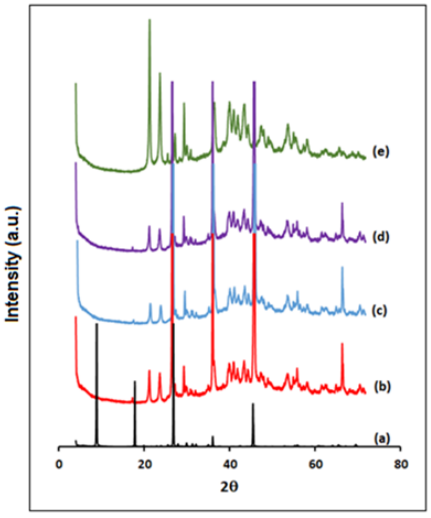

Figure 6. XRD patterns of: (a) Mica125, (b) WP/Mica125, (c) WP/Mica125US30, (d) WP/Mica125US60 and (e) WP.

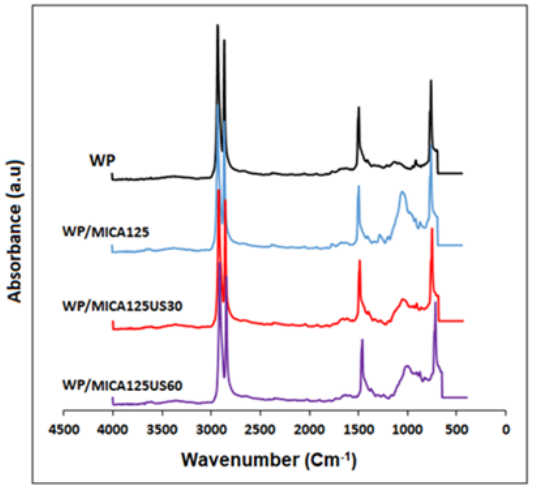

Figure 7. FTIR spectra of WP and WP/Mica composites.

These results indicate that the polymers in the wood plastic residues were mainly polyolefins. The vibrations of the mica group minerals appeared between 1200-500 cm^{-1} for the composite samples. Since the spectra of all composites were very similar, it can be assumed that only physical interactions occurred between WP and muscovite[3,4,7].

4. Conclusions

It was possible to obtain composites of ultrasonicated muscovite and post-industrial wood plastic residues. The ultrasonicated muscovite showed delamination and a slight decrease in particle size, which resulted in improved interaction with and dispersion in the polymeric matrix, with consequent increase in impact resistance for composite samples. Furthermore, ultrasonication did not alter the chemical structure or the crystalline structure of muscovite and wood plastic, and no chemical additives were used in the sonication process or the preparation of composites.

Since both wood plastic and muscovite used in this work are materials with low value and ultrasonication is an eco-friendly treatment method that has proved to be useful to promote delamination of mica and improvement of adhesion in mica/wood plastic composites, our process can be considered efficiente and sustainable to obtain polymer-mineral composites.

5. Acknowledgements

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