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# The influence of Ni/Mg content of synthetic Mg/Ni talc on mechanical and thermal properties of waterborne polyurethane nanocomposites

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## Abstract:

Waterborne polyurethanes (WPU) present interesting properties when compared to their solvent-based counterpart besides being organic solvent free. WPU also present some drawbacks such as low thermal and mechanical properties. The goal of this work was to synthesize and characterize new synthetic talc in a gel form with different magnesium (Mg) and nickel (Ni) ratios in their chemical structure  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  with  $0 < x < 1$  and to evaluate their influence on mechanical and thermal properties when used as filler in WPU matrix in order to obtain new nanocomposites as well. WPU/STMg<sub>x</sub>Ni<sub>y</sub> nanocomposites were prepared by physical mixing and characterized by Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Atomic force microscopy (AFM) and Mechanical Dynamic Analysis (DMTA). Improvements in nanocomposites mechanical properties in relation to pristine WPU matrix was observed for samples with higher synthetic talc content. The variation of the amount of Mg and Ni in synthetic talc composition altered the storage and loss modules results being higher for nanocomposites obtained with synthetic talc samples with higher Ni content in their compositions. Tg varied according to synthetic talc content. Synthetic talc with different metal content in their composition changes WPU nanocomposites thermal and mechanical properties. These fillers can be used to design nanocomposites with desired applications.

**Key words:** Waterborne polyurethane; Synthetic STMg<sub>x</sub>Ni<sub>y</sub> talc; Nanocomposites.

## Introduction

Polyurethanes (PU) are engineering materials finding different industrial application. In general PU are synthesized using organic solvents [1]. Due to environmental safety, organic solvents are gradually being replaced by water since the 1960s [1]–[5]. This solvent replacement initiative besides the manufacturing cost reduction helps to reduce volatile organic compounds (VOCs) emission into the environment [6]. WPU can find several application niches as adhesives, paint additives, coatings, sealants, medicaments, membranes, among others [7], [8]. WPU present interesting properties when compared to their solvent-based counterpart, such as transparency, flexibility, abrasion resistance, non-flammability and high adhesion. The main disadvantage is related to low thermal and mechanical resistance [9]–[11]. Aiming to improve these properties the addition of nanofillers has been studied. Literature describes the incorporation of silica nanohybrids [12], TiO<sub>2</sub> [13], cellulose nanofillers [14], Fe<sub>2</sub>O<sub>3</sub> [15], Ni-Zn [16], [17], SiO<sub>2</sub> [18], carbon nanofillers [19], clays and carbon nanotubes [20], Ni<sub>0.3</sub>Zn<sub>0.5</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticles [21], synthetic talc [22], ferrite nanoparticles [23]–[25], ZnO [24], graphite [26], graphene oxides [27], nanoclay [28], [29]functionalized clays[30].

Talc is a layered magnesium phyllosilicate mineral of chemical formula Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> being used as nanofiller for composite materials preparation [32], [33] in order to reduce production cost, enhance physical and chemical properties and provide new functionality to polymer matrix [34], [35]. Crystal-chemistry of talc structure can be modified by fully or partly replacing the Mg metal by other metals. Temperature, time and pressure can also be controlled during hydrothermal synthesis in order to obtain the desired structure [36], [37]. Unlike hydrophobic natural talc, synthetic talc can be obtained in a gel form due to their hydrophilic character facilitating their use in water-based polymer matrix nanocomposite synthesis [32], [33], [36], [38]. Due to this myriad of possible synthetic talc structures and properties these new materials can be used as fillers for solvent-based polyurethane nanocomposites [39], [40] as well as for WPU nanocomposites [41] preparation resulting in fluorescent nanocomposites [41], magnetic nanocomposites [23], [42] among others possibilities.

The main goal of this work was the synthesis and characterization of new synthetic talcs in a gel form substituting the magnesium by nickel in the percentages of 25%, 50% , 75% and 100% in their chemical structure Si<sub>4</sub>(Mg<sub>x</sub>Ni<sub>1-x</sub>)<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> with 0<x<1. Yet, the effect of Ni content on the nanocomposite WPU/synthetic talc formation, thermal and mechanical properties was evaluated.

## 2. Materials and Methods

### WPU synthesis

WPU was prepared by prepolymer method. The dispersion preparation occurred in two steps. The first was the prepolymer formation by the mixture of linear polyester polyol, isofurone diisocyanate (IPDI) (NCO/OH=1,7) and dimethyl propionic acid (DMPA) solubilized in n-methylpyrrolidone. The mixture was kept in a closed system, at 85°C, under mechanical stirring (500rpm) for 1h. Free NCO content was monitored by titration with N-dibutylamine (based on the ASTM 2572 standard). Once the desired free NCO content was reached the temperature was reduced and maintained at 60°C and triethylamine (TEA) was added. TEA addition was performed under mechanical stirring at 500rpm for 15 minutes in order to neutralize the ionic groups generated by DMPA addition. The second reaction step was the

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neutralized prepolymer dispersion in a mixture of water /chain extender (hydrazine) under mechanical stirring (250 - 500rpm) at 10°C of temperature for 30 minutes. The dispersion solid content was 33%.

### Synthetic talc synthesis

$\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  synthetic talc with  $0 < x < 1$  was obtained by hydrothermal reaction as previously described [32], [43], [44]. The reactants ratio used in synthetic talc synthesis were based on the chemical formula of natural talc ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ). When using different metals the reactants are mixed in stoichiometric proportions based on the chemical formula: ( $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  with  $0 < x < 1$ ,  $\text{Si}/\text{Mg-Ni} = 4/3$ ) [45], [46]. In order to synthesize the talc-Ni the substitutions of magnesium by nickel were performed from 25% to 100%, as shown in Table 1.

Table 1. Talc chemical formulas according to the substitution percentage of the Mg cation for Ni.

Replacement ratio	Talc Chemical Formula	Adopted nomenclature
0%	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	-----
25%	$\text{Mg}_{2,25}\text{Ni}_{0,75}\text{Si}_4\text{O}_{10}(\text{OH})_2$	ST25Ni
50%	$\text{Mg}_{1,5}\text{Ni}_{1,5}\text{Si}_4\text{O}_{10}(\text{OH})_2$	ST50Ni
75%	$\text{Mg}_{0,75}\text{Ni}_{2,25}\text{Si}_4\text{O}_{10}(\text{OH})_2$	ST75Ni
100%	$\text{Ni}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	ST100Ni

To synthesize the talc samples the Si source was sodium metasilicate pentahydrate ( $\text{NaSiO}_3 \cdot 5\text{H}_2\text{O}$ ), the Mg source was magnesium acetate tetrahydrate ( $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) and the Ni source was nickel acetate tetrahydrate ( $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ). Sodium acetate ( $\text{CH}_3\text{COONa}$ ) was used as catalyst for all reactions. Two solutions were prepared, first the Si source was solubilized in water and mixed to the catalyst. The Mg and/ or Ni source (according to desired percentage) was solubilized in water and mixed with acetic acid ( $\text{CH}_3\text{COOH}$ ). The two solutions were mixed under magnetic stirring and ultrasonicated until a homogeneous mixture was obtained. The  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  synthetic talcs were hydrothermally synthesized at 300°C for 6h under 86 bar of pressure. After the reaction the obtained synthetic talc was withdrawn from the reactor in the gel form [36], [37].

### WPU nanocomposites preparation

WPU nanocomposites were prepared by physical mixtures. A 100g sample of WPU was placed under mechanical stirring (2000 rpm) for 30 minutes. The fillers ST25Ni, ST50Ni, ST75Ni e ST100Ni were added in different contents of 1% and 10% in relation to WPU weight. At the end, films of 70µm of thickness were produced by molding.

### Synthetic talc and nanocomposites characterization

WPU, synthetic talc and WPU nanocomposites films (thickness of 0.01mm) were characterized by Fourier transform infrared spectroscopy/universal attenuated total reflectance (FTIR/UATR, PerkinElmer FTIR spectrometer model Spectrum100). The nanocomposites spectra acquisition data were performed in absorption mode in the range of  $4000 - 400\text{cm}^{-1}$  and for synthetic talc in the range of  $10000 - 400\text{cm}^{-1}$ . WPU nanocomposites patterns for X-ray

diffraction (XRD) were recorded on a Shimadzu XRD-7000 diffractometer equipment with CuK $\alpha$  Bragg-Brentano  $\theta$ - $\theta$  geometry, between 5 and 80 degrees with a step size of 0.02 degrees, current of 40 kV and voltage of 30mA. The talc standards were recorded in INEL CPS 120 powder diffractometer with CoK $\alpha$ 1 + 2 radiation between 0.334 and 127,206 $^{\circ}$ 2 $\theta$ . Thermogravimetric (TGA) analyzes of WPU and its nanocomposites were performed using a SDT equipment (TA Instruments model Q600). The tests were performed in a temperature ranging from 25 $^{\circ}$ C to 800 $^{\circ}$ C with a heating rate of 20 $^{\circ}$ C/min under constant N $_2$  flow. The TGA analyzes were performed in triplicate. WPU samples and nanocomposites were analyzed by Mechanical Dynamic Analysis (DMTA-TA Instruments Model Q800) for thermomechanical tests. Stress/strain tests were performed at 25 $^{\circ}$ C. Loss modulus, storage modulus and tan  $\delta$  were acquired utilizing a ramp from -80 to 80  $^{\circ}$ C. Mechanical tests were performed using rectangular films (0.15 mm thick, 12 mm long and 7.0 mm wide). The Young modulus of the materials was determined according to ASTM D638. Analyzes were performed in triplicate. Scanning Electron Microscopy (SEM) images were emitted by scattered retroelectronic (BSE) mode on PHILIPS XL30 equipment, using gold for samples metallization. The films used for this characterization were of approximately 0.2mm thick; Transmission Electron Microscopy (TEM) was used to determine the particle size and morphology of nanocomposites. The samples were cryomicrotomed and analyzed on a Tecnai G2 T20 FEI operating at 200 KV. Atomic force microscopy (AFM) analyzes were performed in peak touch mode using a PT Bruker Dimension Icon equipped with a TAP150A probe (Bruker, resonance frequency 150 kHz and spring constant of 5 N / m). The equipment was calibrated prior to sample measurements. The scanned area of the images was 5 x 5  $\mu$ m $^2$  with a resolution of 512 frames per area (LabCEMM/PUCRS).

### 3. Results and Discussion

#### 3.1 FTIR Analysis

Infrared analyzes for synthetic talc Si $_4$ (Mg $_x$ Ni $_{1-x}$ ) $_3$ O $_{10}$ (OH) $_2$  samples with different Ni contents are shown in Figures 1 and 2.

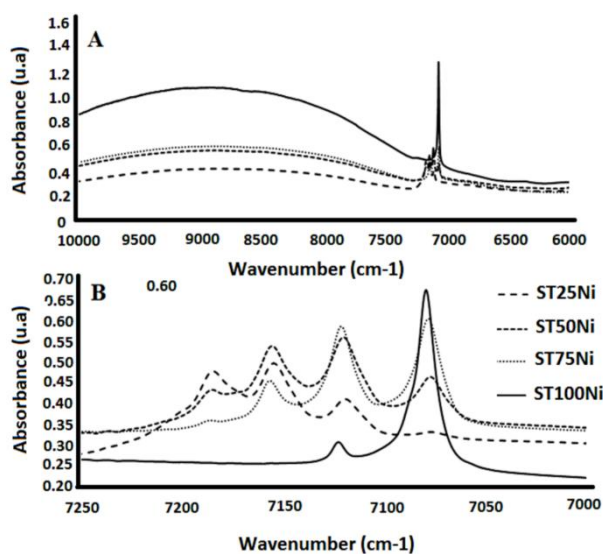


Figure 1. Infrared Spectra for Si $_4$ (Mg $_x$ Ni $_{1-x}$ ) $_3$ O $_{10}$ (OH) $_2$  synthetic talc (A) in the range from 10000cm $^{-1}$  to 6000cm $^{-1}$ ; (B) range from 7250cm $^{-1}$  to 7000cm $^{-1}$ .

Infrared spectrum for phyllosilicates undergoing partial replacement of Magnesium (Mg) by another divalent metal species shows a division in the hydroxyl stretch-up to four peaks, depending on the substitution degree [47]–[50]. The spectra presented in Figure 1(A) and (B) shows from high to low frequencies a random distribution of two metallic species (Mg and Ni), being the four bands related to the OH ion vibrating near the  $3\text{Mg}^{+2}$ ,  $2\text{Mg}^{+2}+\text{Ni}^{+2}$ ,  $\text{Mg}^{+2}+2\text{Ni}^{+2}$  and  $3\text{Ni}^{+2}$  species located in the mineral octahedral layer [47]. The hydroxyl stretch division is related to the M-OH bond strength change. Increasing Mg cation substitution of the original mineral structure decreases band division [47].

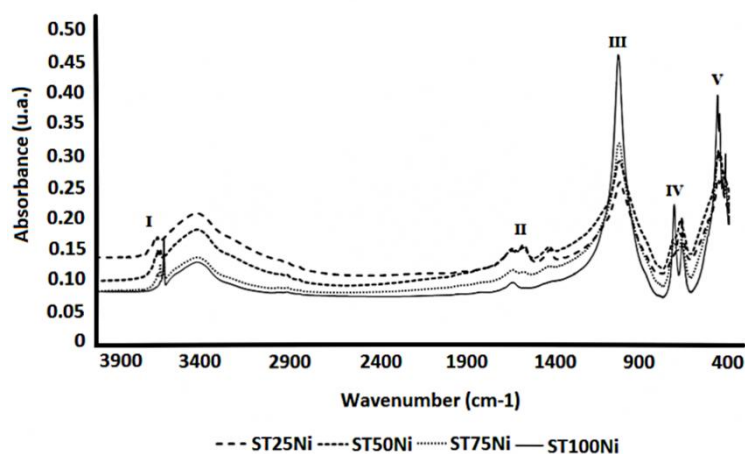


Figure 2. Infrared Spectra for  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  synthetic talc.

Spectra shown in Figure 1 (B) and 2 (I) stands for the second and the first frequency of the OH bounded to Mg and Ni respectively according to the substitutions degree. The OH stretching for a talc presenting 100% of Mg cations substituted for Ni predicts the first frequency at  $3627\text{cm}^{-1}$  and the second at  $7080\text{cm}^{-1}$  attributed to OH of  $\text{Ni}_3\text{OH}$  molecule. For a talc presenting 75% of Mg cations substituted for Ni, the frequencies at  $3647\text{cm}^{-1}$  and  $7122\text{cm}^{-1}$  are attributed to OH of  $\text{MgNi}_2\text{OH}$  molecule. For a talc with 25% of Mg cations substituted for Ni the frequencies at  $3661\text{cm}^{-1}$  and  $7154\text{cm}^{-1}$  are related to OH of  $\text{Mg}_2\text{NiOH}$  molecule [47], [49], [50].

The frequencies at  $3676\text{cm}^{-1}$  and  $7185\text{cm}^{-1}$  are equivalent to a mineral structure presenting in its composition the molecule  $\text{Mg}_3\text{OH}$  [47], [49]–[51]. These bands were identified in the spectra of synthetic talcs ST25Ni and ST50Ni presenting a lower Ni percentage when compared to ST75Ni and ST100Ni. As we can see from Figure 2 (II) frequencies in the region of  $1700\text{cm}^{-1}$  to  $1300\text{cm}^{-1}$  are present in all synthetic talcs spectrum related to characteristic OH band deformation due to the presence of water [52]. In Figure 2 (III) one can observe an overlap of Si-O and Si-O-Si bands around  $1025\text{cm}^{-1}$  for ST25Ni, ST50Ni and ST75Ni and at  $1030\text{cm}^{-1}$  for ST100Ni [43], [51]–[53]. Frequencies in the region at  $800\text{cm}^{-1}$ –  $600\text{cm}^{-1}$  are characteristic of free OH in the synthetic talcs structure. As seen in Figure 2 (IV) the frequencies at  $710\text{cm}^{-1}$  to  $666\text{cm}^{-1}$  are present for the four samples of synthetic talc [43], [51]. The bands in the region of  $470\text{cm}^{-1}$ –  $420\text{cm}^{-1}$  presented in Figure 2 (V) represent the Si-O-Si overlap and the translation of the OH groups with the oxygen atoms of the octahedral sheet [43], [51], [52].

Nanocomposites infrared spectra (Fig. 3) present polyurethane characteristic bands: at  $2936\text{cm}^{-1}$  C-H stretching band of urethane  $\text{CH}_3$  and  $\text{CH}_2$  groups; at  $1532\text{cm}^{-1}$  attributed to H-N group and at  $1245\text{cm}^{-1}$  attributed to the N-C stretch [39], [40], [42]. Yet, it is possible to see a band at  $1630\text{cm}^{-1}$  for all nanocomposites attributed to H-O-H band of

intercalated water in the talc leaves [54] or it may also be related to the Si-O vibrations of the  $\text{SiO}_4$  molecule present in talc structure [51]. The vibration band at  $1020\text{cm}^{-1}$  undergoes changes in intensity while increasing synthetic talc content in nanocomposites being attributed to Si-O and Si-O-Si from synthetic and natural talc [43], [51]–[53]. The appearance of the band at  $1630\text{cm}^{-1}$  and the difference in band intensity at  $1020\text{cm}^{-1}$  corroborates nanocomposite formation.

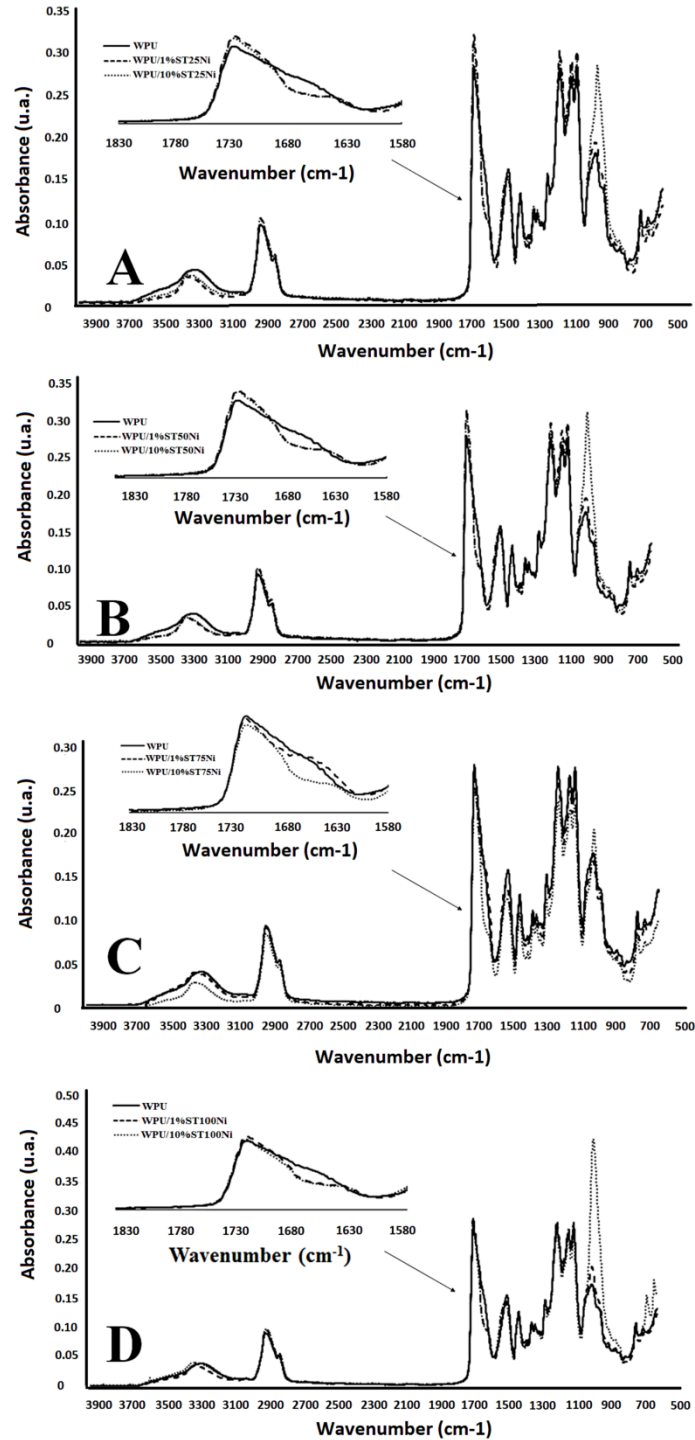


Figure 3. Infrared Spectra of (a) WPU 1%ST25Ni and WPU10%ST25Ni, (b) WPU1%ST50Ni and WPU10%ST50Ni, (c) WPU 1%ST75Ni and WPU10%ST75Ni and (d) WPU 1%ST100Ni and WPU10%ST100Ni.

### 3.2 DRX and TEM Analysis

Figure 4 shows the values of the inter-reticular distance ( $d$ ) of peaks 001(9.5Å), 002(4.6 Å), 003(3.1 Å), 004 (2.54 Å) and 060(1.5 Å) characteristic of  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  synthetic talc samples [36]. As the Ni amount increases in synthetic talc samples the peaks become more intense indicating an increase in synthetic talc crystallinity [55].

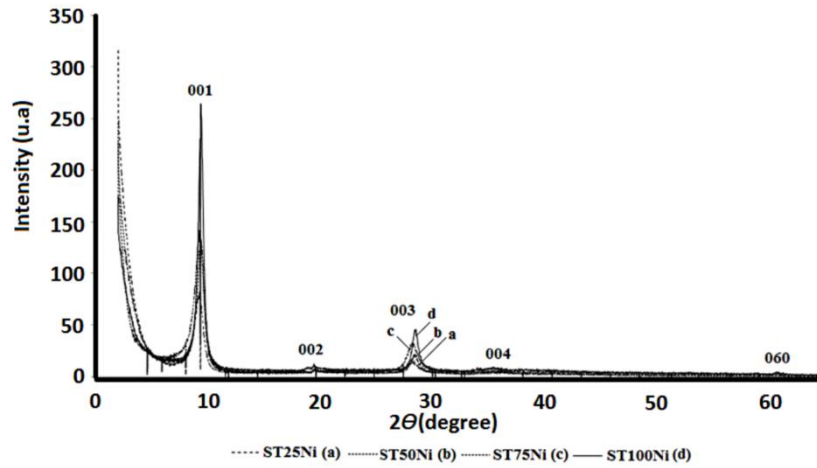


Figure 4. X-ray diffraction patterns for  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  synthetic talc.

Figure 5 presents XRD spectra of the WPU/  $\text{STMg}_x\text{Ni}_y$  nanocomposites.

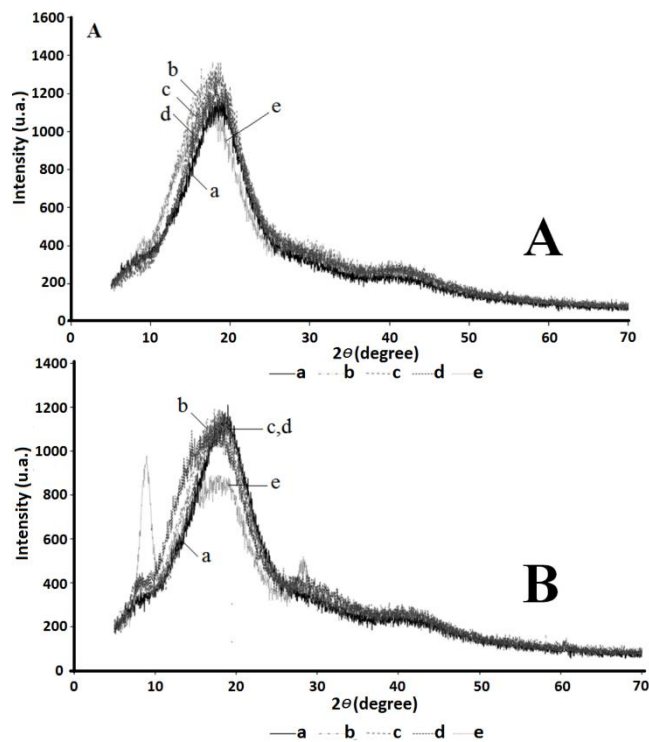


Figure 5. X-ray diffraction patterns for WPU/  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  nanocomposites (A) WPU/1% /  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  [a-WPU pristine; b-WPU/1%ST25Ni; c-WPU/1%ST50Ni; d-WPU/1%ST75Ni; e-WPU/1%ST100Ni]. (B)



WPU/10% /  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  [a-WPU pristine; b-WPU/10%ST25Ni; c-WPU/10%ST50Ni; d-WPU/10%ST75Ni; e-WPU/10%ST100Ni].

From WPU nanocomposites (1% and 10% of synthetic talc) diffractograms one can observe an intensity decrease for peaks at  $2\theta = 10^\circ - 28^\circ$ , associated to PU amorphous phase of flexible segment of WPU chain when compared to pristine WPU [56]. For nanocomposites with 10% of filler this behavior is more accentuated. The same behavior was observed by Lei L. [27] for WPU/AEAPTMS samples indicating a good interaction filler/polymeric matrix. The appearance of peaks at  $2\theta = 28^\circ$  and  $2\theta = 41^\circ$  with the addition of 1% of synthetic talc referring to pristine talcs planes 003 and 004 is also observed [22], [23], [36]. With the addition of 10% of synthetic talc, peaks at  $2\theta = 9^\circ$  and  $2\theta = 61^\circ$  also appear, which are characteristic of pristine talc planes 001 and 060 [36], [37].

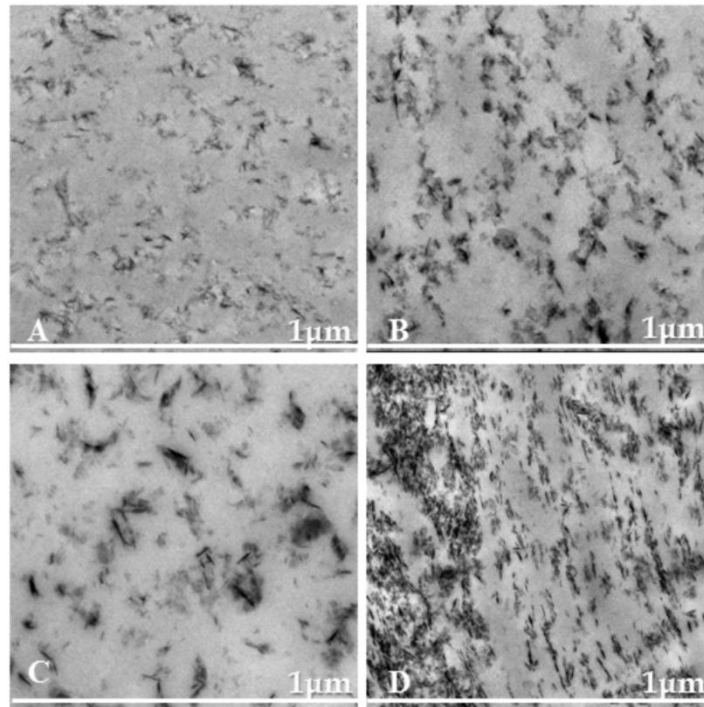


Figure 6: TEM of WPU/  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  10% nanocomposites samples. (A) WPU/ST25Ni; (B) WPU/ST50Ni; (C) WPU/ST75Ni; (D) WPU/ST100Ni.

WPU nanocomposites TEM micrographs are shown in Figure 6. Nanocomposites obtained with talc containing lower Ni content (ST25Ni and ST50Ni) presents the filler predominantly in an exfoliated/intercalated form [36]. The sample with 75% of Ni (ST75Ni) presents the filler in an intercalated manner while the sample with 100% of Ni (ST100Ni) is mainly non intercalated as already observed in a previously work [40]. Nanocomposite obtained with talc with 100% of Ni content (ST100Ni) shows an organization into the polymeric matrix (see Figure 6 (D)). As we will see in mechanical properties section this filler/matrix interaction/organization will positively interfere in mechanical properties.

### 3.3 Thermal Analysis

TGA results can be observed in Table 2. Samples presented two degradation stages: the first stage is related to hard segment degradation and the second one to soft segment degradation. WPU nanocomposites prepared with the addition of 1% of synthetic talc presented similar degradation temperatures when compared to pristine WPU. With addition of 10% of ST25Ni and ST50Ni synthetic talc the degradation temperatures slightly increase when compared to pristine WPU. Nanocomposites obtained with ST75Ni and ST100Ni showed similar degradation values to pristine WPU. This behavior may be associated with Ni amount in synthetic talc composition as observed for nanocomposites obtained with synthetic PU/synthetic talc-Ni100%. Literature reported that the addition of 5 %wt of ST100Ni decreases the nanocomposites thermal stability due to charge-charge interaction [40]. The particles in a composite must be well distributed to increase film thermal resistance [57].

Table 2. TGA results for WPU and its nanocomposites.

Sample	T <sub>onset</sub> (°C)	T <sub>máx 1</sub> (°C)	T <sub>máx 2</sub> (°C)
WPU	305	342	383
WPU/ST25Ni 1%	297	335	389
WPU/ST50Ni 1%	303	344	385
WPU/ST75Ni 1%	304	340	387
WPU/ST100Ni 1%	301	345	380
WPU/ST25Ni 10%	316	373	439
WPU/ST50Ni 10%	326	380	466
WPU/ST75Ni 10%	301	340	390
WPU/ST100Ni 10%	305	346	465

### 3.4 Mechanical Analysis

Mechanical properties are presented in Figures 7 and 8 and Table 3. It is possible to observe that for talc content of 10% an increase in Young's Modulus values was observed, [Fig. 7B; Table 3] (20.5MPa for pristine WPU and 46.7MPa for WPU/ ST100Ni). This behavior can be associated with filler/matrix cohesive energy occurring due to the strong interaction by hydrogen bonds [42], [58] and also due to the filler organization inside polymeric matrix.

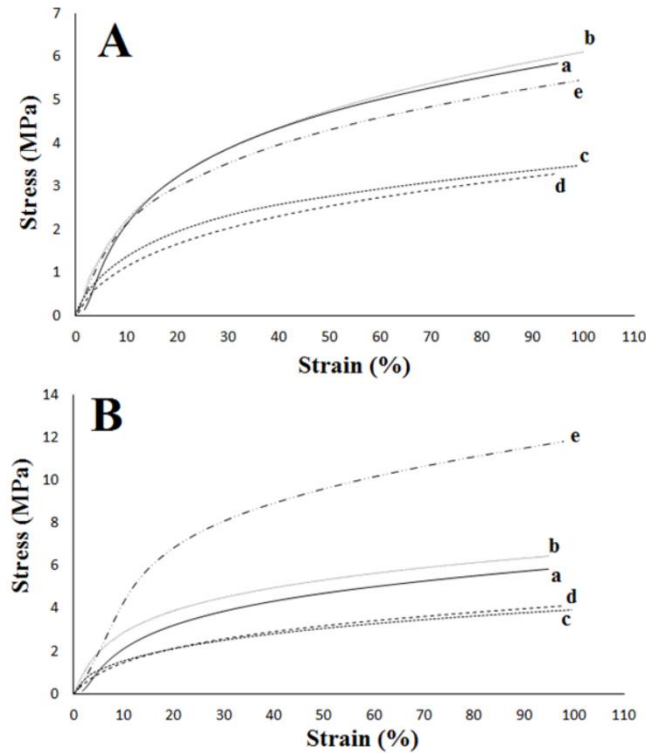


Figure 7. DMA WPU/Si<sub>4</sub>(Mg<sub>x</sub>Ni<sub>1-x</sub>)<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> nanocomposites. (A) WPU/1% Si<sub>4</sub>(Mg<sub>x</sub>Ni<sub>1-x</sub>)<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> [a-WPU pristine; b-WPU/1%ST25Ni; c-WPU/1%ST50Ni; d-WPU/1%ST75Ni; e-WPU/1%ST100Ni]. (B) WPU/10% Si<sub>4</sub>(Mg<sub>x</sub>Ni<sub>1-x</sub>)<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> [a-WPU pristine; b-WPU/10%ST25Ni; c-WPU/10%ST50Ni; d-WPU/10%ST75Ni; e-WPU/10%ST100Ni].

WPU nanocomposites with 1% of synthetic talc [Fig. 7A, Table 3] showed Young modulus values similar to the pristine polymeric matrix. Nanocomposites WPU/ST50Ni and WPU/ST75Ni with 1% and 10% of synthetic talc presented Young modulus values inferior when compared to pristine matrix. This may be associated with filler/filler interaction for these nanocomposites. Similar behavior was observed by Mohammadi Abbas [59], in functionalized PU/Fe<sub>2</sub>O<sub>3</sub> nanocomposites.

Table 3. DMA results for WPU and its nanocomposites.

Sample	Stress (MPa)	Strain (%)	Young Modulus (MPa)
WPU	5.9±0.7	94.5±0.7	20.5±1.6
WPU/ST25Ni 1%	5.8±0.4	97.8±1.7	22.5±1.6
WPU/ST50Ni 1%	3.7±0.5	97.8±1.2	14.0±2.0
WPU/ST75Ni 1%	3.7±0.6	94.9±0.4	11.3±2.7
WPU/ST100Ni 1%	5.4±0.1	99.8±0.1	20.9±1.2
WPU/ST25Ni 10%	6.4±0.6	96.7±1.5	30.1±2.2
WPU/ST50Ni 10%	4.4±0.4	99.6±0.2	16.6±0.3

WPU/ST75Ni 10%	4.4±0.4	97.6±0.5	16.4±3.2
WPU/ST100Ni 10%	11.6±1.0	97.7±0.5	46.7±3.9

Nanocomposites sample strain value were slightly higher when compared to pristine matrix indicating a good dispersion of the synthetic talc into the WPU matrix [40], [60]. The influence of filler good dispersion, organization into the polymeric matrix and chemical composition is also evidenced by the stress values of the nanocomposites prepared with synthetic talc with different Ni content and 10% of synthetic talc addition. Compare samples with 50% and 100% of Ni in their chemical structure (stress value of sample WPU/ST50Ni 10% of 4.4±0.4 MPa with sample WPU/ST100Ni 10% of 11.6±1.0 MPa) showing that synthetic talc chemical structure can have an important influence in WPU nanocomposite mechanical properties. It is well known that nanocomposites obtained with high synthetic talc content can present important synthetic talc/synthetic talc interaction resulting in a brittle sample [57], [61]. Dos Santos, [23] described that nanocomposites obtained with high amounts of synthetic talc (40%) can produce nanocomposite films with high mechanical properties [23]. These results may be associated with the nanocomposite preparation method. Physical mixture method result in nanocomposites with more efficient synthetic talc/polymer interaction when compared to the in situ method [22], [23]. The in situ method could facilitate the filler/matrix crosslink due to the chemical reaction [39], [40]. The results of the storage ( $E'$ ) and loss ( $E''$ ) modules as well as  $\tan \delta$  for pristine WPU and nanocomposites are shown in figure 8.

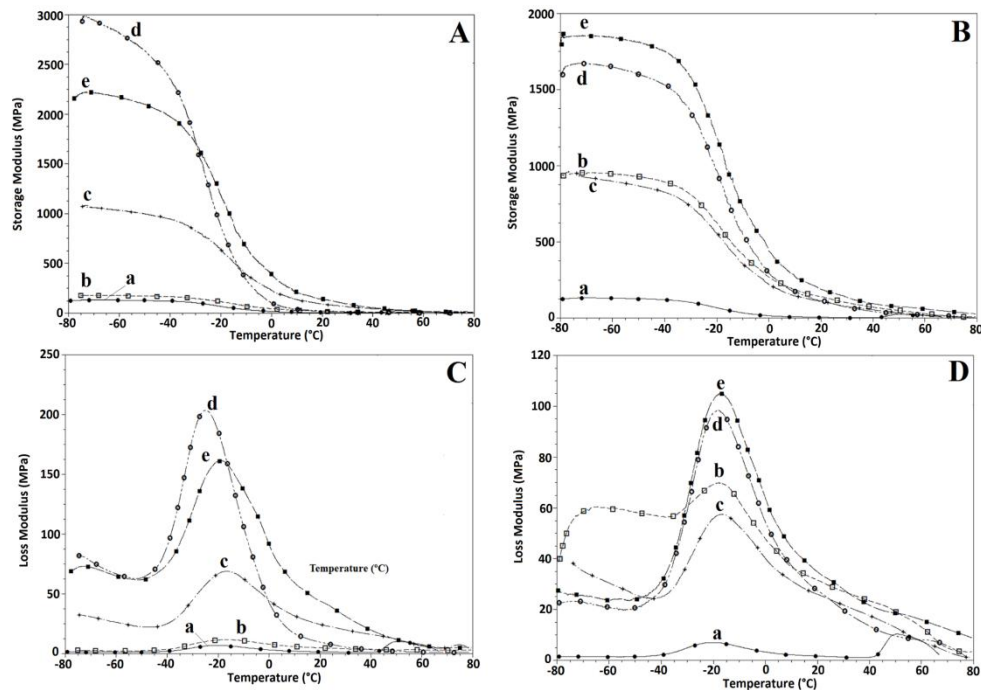


Figure 8. (A) Storage Modulus WPU/1%  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  and (C) Loss Modulus WPU/1%  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$ ; [a-WPU pristine; b-WPU/1%ST25Ni; c-WPU/1%ST50Ni; d-WPU/1%ST75Ni]. (B) Storage Modulus WPU/10%  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  and (D) Loss Modulus WPU/10%  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$ . [a-WPU pristine; b-WPU/10%ST25Ni; c-WPU/10%ST50Ni; d-WPU/10%ST75Ni].

Storage modulus ( $E'$ ) [Fig.8A and B] values increase significantly with filler content increasing. The Ni content in synthetic talc composition also increases  $E'$  indicating that the presence of Ni improves the interaction of synthetic talc/WPU matrix [31], [62]. Comparing the WPU/ST25Ni nanocomposites (1%= 171 MPa and 10%= 912 MPa) and the

WPU/ST100Ni nanocomposites (1%= 2086 MPa and 10%= 1814 MPa) with pristine WPU (128 MPa) it is observed the influence of filler Ni content in storage modulus values. In loss modulus analysis (Fig. 8C and D), it was noticed the presence of two peaks for pristine WPU (7 MPa and 10 MPa), related to flexible and rigid segments of polymeric matrix respectively [63]. With synthetic talc addition (1%) the second peak shift as for ST25Ni (3 MPa and 12 MPa) and ST50Ni (7MPa and 69MPa). For ST75Ni (203 MPa) and ST100Ni (161 MPa) the energy of the first peak increases significantly and the second peak tends to disappear. The disappearance of the second peak shows that the interaction of synthetic talc with higher Ni content in the composition is more effective. This interaction takes place in the rigid region of the WPU matrix. With the synthetic talc addition of 10% the second peak disappeared for all nanocomposites.

Loss modulus curves (fig. 8C – D) show a transition peak. This peak is usually assigned to the soft segments of WPU matrix. This change in loss modulus and Tg values (WPU = 237 MPa at -24 °C; WPU/ST100Ni 1%= 158 MPa at -19 °C and WPU/ST100Ni 10%= 102 MPa at -18 °C) could be related to the good incorporation and distribution of the fillers into WPU chains [64]. Higher values for storage modulus, loss modulus and Tg peak indicated strong adhesion of the fillers into the WPU matrix, as previously reported by our group [22].

### 3.5 Morphological Analysis

Figure 9 presents the FESEM micrographs for pristine WPU and for the nanocomposites with addition of 1% and 10% of  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  synthetic talcs.

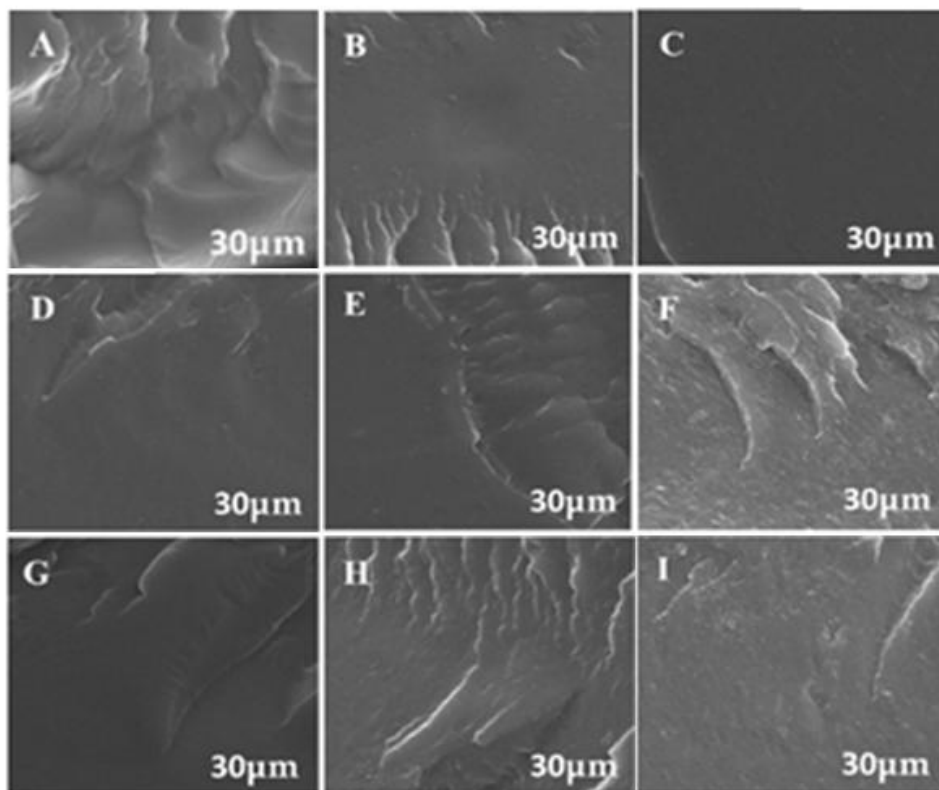


Figure 9. FESEM of film surface(A) WPU pristine. (B) From to (E) samples WPU/  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  1% nanocomposites - (B) WPU/ST25Ni, (C) WPU/ST50Ni, (D) WPU/ST75Ni and (E) WPU/ST100Ni. (F) From to (I) WPU/  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  10% nanocomposites – (F) WPU/ST25Ni, (G) WPU/ST50Ni, (H) WPU/ST75Ni and (I) WPU/ST100Ni.

All samples present cracks. WPU nanocomposites images show rough surfaces similar to pristine WPU matrix. FESEM images indicate a homogeneous filler distribution for all nanocomposites showing that the WPU may be interacting with the filler [27]. Filler good distribution into the polymeric matrix is one of the factors interfering in nanocomposite mechanical properties, as observed by Peng, L. [65] for WPU nanocomposites with a natural fibrillary mineral clay.

Figure 10 shows AFM images for all samples of nanocomposites and pristine WPU.

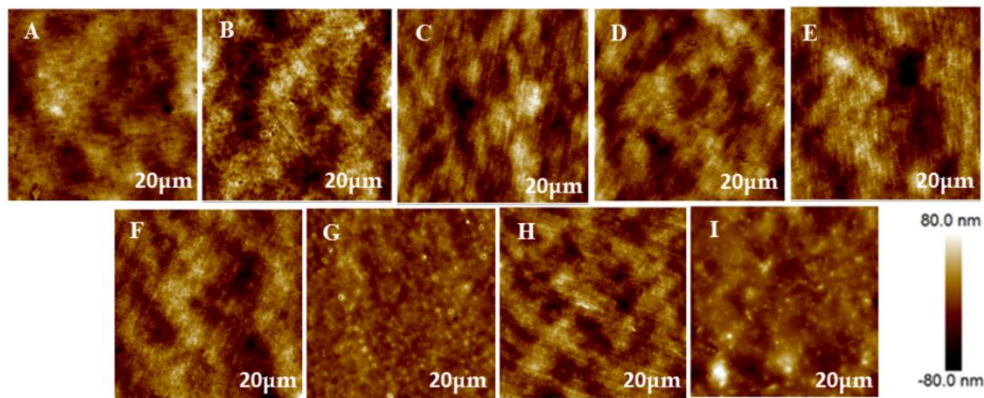


Figure 10. AFM images. (A) WPU pristine. (B) to (E) samples WPU/1%  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  nanocomposites - (B) WPU/ST25Ni, (C) WPU/ST50Ni, (D) WPU/ST75Ni and (E) WPU/ST100Ni. (F) to (I) WPU/10%  $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  nanocomposites – (F) WPU/ST25Ni, (G) WPU/ST50Ni, (H) WPU/ST75Ni and (I) WPU/ST100Ni.

WPU matrix presents dark and bright areas corresponding to amorphous (flexible segments) and crystalline domains (rigid segments), respectively [66]. With synthetic talc addition rearrangements can take place into the polymeric matrix structure depending on the synthetic talc/WPU interaction. For higher filler content the interaction synthetic talc/ polymer matrix becomes more intense changing the polymer matrix organization as seen in Figure 10. Increasing Ni content in the synthetic talc chemical structure a tendency of a small separation among hard and soft segments is also observed and could be related with polymer chain reorganization due to the interaction of synthetic talc/polymer matrix taking place in the rigid region of the WPU matrix as observed in the Loss modulus test. Yet, the synthetic talc/ synthetic talc interaction can occurs with higher filler contents [23]. In samples with 10% of synthetic talc it is possible to visualize more intense bright spots on the matrix surface attributed to agglomerated particles in synthetic talc/ synthetic talc form [25].

#### 4. Conclusions

WPU/ $\text{Si}_4(\text{Mg}_x\text{Ni}_{1-x})_3\text{O}_{10}(\text{OH})_2$  nanocomposites were prepared by physical mixing. Synthetic talc presents different chemical composition in relation to Mg and Ni content occurring in the octahedral sheets of synthetic talc structure. FTIR, DRX and TEM analyses demonstrate the good synthetic talc/WPU matrix interaction. FESEM and AFM showed a homogeneous distribution of talc particles for all samples. Improvements in nanocomposites mechanical properties in

relation to the pristine WPU matrix was observed for samples with higher synthetic talc content. The variation of the amount of Mg and Ni in synthetic talc composition altered the storage and loss module results being higher for nanocomposites obtained with synthetic talc with higher Ni content in their compositions. The T<sub>g</sub> varied according to synthetic talc content. Synthetic talc with different metal content in their composition may alter thermal and mechanical properties of WPU nanocomposites and can thus be designed for several applications.

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### Conflict of Interest Statement

The authors declare that there is no conflict of interest

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