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Melt-processing of bionanocomposites based on ethylene-co-vinyl acetate and starch nanocrystals.

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ABSTRACT

Starch nanocrystals (SNCs) were successfully synthesized by acid hydrolysis of waxy barley starch and were characterized by X-ray diffraction, scanning and transmission electron microscopy. Nanocomposites based on ethylene-co-vinyl acetate (EVA) and SNCs were produced by melt-processing using a microextruder. Interesting is to note that SNCs do not lose their crystalline nature during melt-processing. Moreover, the mechanical and thermal properties of the neat matrix were improved by the addition of SNCs thanks to the strong hydrogen bonding between the nanofillers surface and the acetate groups of the matrix. The introduction of 2 wt.% and 5 wt.% of SNCs into the matrix, lead to an increase of its elastic modulus of about 50 % and 100 %, respectively. Moreover, the addition of SNCs provoked an increase of the thermal stability of about 10 °C respect to the neat matrix. These results clearly revealed the possibility to introduce SNCs in a polymeric matrix by extrusion enabling to reach materials with

enhanced mechanical and thermal properties due to beneficial hydrogen bonding between SNCs and EVA.

Highlights

- Hydrogen bonds between acetate groups and -OH groups of SNCs surface are formed;
- Good dispersion of SNCs into the EVA matrix thanks to the physical interactions;
- Hydrogen bond interactions lead to improved mechanical and thermal properties;

Keywords: starch nanocrystals, solvent-free process, melt-processing, EVA, hydrogen bonding.

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1. Introduction

In the last several years, polymeric nanocomposites based on bionanofillers have attracted both academic and industrial attentions due to the increasing interest on designing new “green” bionanocomposites based on renewable nanofillers (Darder, Aranda, & Ruiz-Hitzky, 2007; Hebeish, El-Rafie, El-Sheikh, & El-Naggar, 2014). In particular, nanowhiskers and nanocrystals obtained from natural polymers have been applied to reinforce biodegradable or non-biodegradable polymeric matrix. In general,

these kind of natural nanofillers are produced by acid hydrolysis of natural polysaccharides, such as cellulose, chitin and starch and they are obtained as aqueous suspensions (Le Corre, Bras, & Dufresne, 2010; Lin, Huang, Chang, Anderson, & Yu, 2011; Navarro-Baena, Kenny, & Peponi, 2014). For this reason, most investigations have focused on the use of hydrosoluble (Chen, Cao, Chang, & Huneault, 2008) (or at least hydrodispersible) or latex-form polymers (Rajisha, Maria, Pothan, Ahmad, & Thomas, 2014) as matrix in order to reach good fillers dispersion. In general, due to their polar character, to reach a good dispersion of polysaccharides nanocrystals into apolar polymeric matrices is a very interesting challenge (Peponi, Puglia, Torre, Valentini, & Kenny, 2014). Polysaccharide nanocrystals possess a reactive surface related with hydroxyl groups, providing the possibility of extensive chemical modifications that open interesting possibilities for nanocomposite processing (Goffin, Habibi, Raquez, & Dubois, 2012; Haaj, Thielemans, Magnin, & Boufi, 2014; Hebeish et al., 2014; Jiahui et al., 2008; Labet, Thielemans, & Dufresne, 2007; Valentina Sessini et al., 2018).

Starch is certainly one of the most versatile biodegradable materials for potential use in polymer technology. Indeed, it can be converted into chemicals for the production of synthetic polymers, it can be used for the production of biopolymers through fermentative processes and it can be also hydrolyzed to be a monomer or oligomer. Finally, it can be used as polymeric materials and such as fillers for other polymers (Carvalho, 2013). Interestingly, starch nanocrystals (SNCs) have recently been used as nanofillers in polymeric matrices such as natural rubber (Rajisha et al., 2014), polyvinyl alcohol (Chen et al., 2008), waterborne polyurethanes (Y. Wang, Tian, & Zhang, 2010) and thermoplastic starch (Li et al., 2015; V. Sessini, Arrieta, Fernández-Torres, &

Peponi, 2018; Valentina Sessini, Arrieta, Kenny, & Peponi, 2016) showing increasing reinforcing effects as well as good barrier properties.

Very few studies have been reported concerning the processing of SNCs reinforced nanocomposites by solvent-free methods. Pereda et al. reported the design of nanocomposites based on polyethylene by wrapping the SNCs with a polymer (polyethylene oxide) bearing moieties susceptible to interact physically with the nanoparticle surface and with the apolar matrix. Improved dispersability and reduced thermal degradation of the nanoparticles were observed showing the compatilizing effect of PEO (Pereda, Kissi, & Dufresne, 2014).

Copolymers of ethylene-co-vinyl acetate (EVA) are a class of widely used polymers, with a variety of industrial applications such as flexible packaging, membranes, footwear, biomedical applications, etc. (Peeterbroeck, Alexandre, Jérôme, & Dubois, 2005; Sonia & Dasan, 2013). Interestingly, EVA copolymers are widely used as wood and paper adhesives because of their good interaction with cellulose materials. Indeed EVA is composed of polar vinyl acetate (VA) groups randomly distributed in the apolar ethylene chains. The degree of polarity of EVA increases by increasing the VA content. Interaction between EVA and polar fillers is proportional to the polarity of EVA. In this context, in literature is reported that, the higher is the polarity of EVA, the stronger is the interaction between EVA and silicate as well as cellulose nanowhiskers, leading to a good dispersion of the nanofillers into the polymeric matrix and better reinforcing effect. (Chauve, Heux, Arouini, & Mazeau, 2005; Zhang & Sundararaj, 2004). However, the interactions between EVA and the nanofiller surface are limited by the conformational freedom of the polymer that control the number of acetate groups able to be engaged with hydroxyl groups at the nanofiller surface (Chauve et al., 2005).

Besides, in many cases EVA applications are limited due to its low tensile strength, thermal stability, and high flammability (Bidsorkhi, Adelnia, Pour, & Soheilmoghaddam, 2015; Gao, Beyer, & Yuan, 2005). To overcome these deficiencies, incorporating nanofillers into EVA represents an excellent way to get high-performance EVA-based nanocomposites. At this regard, several investigations have been reported in literature, including the incorporation of graphite oxide (Sengupta, Bhattacharya, Bandyopadhyay, & Bhowmick, 2011), sepiolite (Bidsorkhi, Soheilmoghaddam, Pour, Adelnia, & Mohamad, 2014), montmorillonite (Alakrach, Osman, Noriman, Betar, & Dahham, 2016; Zanetti, Camino, Thomann, & Mülhaupt, 2001), organoclay (Zhang & Sundararaj, 2004), carbon nanotube (Morlat-Therias et al., 2007) and so on.

Despite an extensive search, based on our knowledge, no detailed study on EVA-based nanocomposites reinforced with SNCs processed by solvent-free methods has been reported in literature. For its properties and especially for its polarity, EVA is a perfect candidate to ensure a good dispersion of polar fillers like SNCs providing an interesting platform for the construction of EVA/SNCs nanocomposites with improved properties.

In this work, the preparation of EVA/SNCs nanocomposites by extrusion has been reported and a comprehensive evaluation of SNCs content on mechanical and thermal properties of nanocomposites has been investigated. X-ray diffraction and field emission scanning electron microscopy confirmed the presence of well dispersed SNCs into the EVA matrix. The study clearly revealed the possibility to introduce SNCs in a polymeric matrix by extrusion enabling to reach materials with enhanced mechanical and thermal properties due to beneficial hydrogen bonding between SNCs and EVA.

2. Materials and Methods

2.1 Materials

Commercial EVA copolymer with 19 wt.% VA content was purchased from Exxon Mobil Chemical Company. Waxy barley starch (WBS) was supplied by Lyckeby Culinar AB (Sweden). Sulfuric acid (H₂SO₄) was purchased from Sigma-Aldrich.

2.2 Starch Nanocrystals Synthesis

SNCs were synthesized by acid hydrolysis. WBS granules were mixed with 175 mL of 3.16 M sulfuric acid solution. The suspension was kept under 100 rpm mechanical stirring at 40 °C, using a silicon oil bath for 5 days. The final suspensions were washed by successive centrifugations in distilled water (10,000 rpm for 10 minutes) until reaching neutral pH and redispersed using Ultra Turrax for 5 min to avoid aggregates. The obtained suspensions were filtered on a filter tissue (113 Whatman) and storage at 4 °C (LeCorre, Bras, & Dufresne, 2012). Finally, it was freeze-dried (LIOALFA 6, Telstar) to obtain SNCs powder.

2.3 EVA/SNCs nanocomposites processing

Two nanocomposites with different SNCs content, *i.e.* 2 and 5 wt.%, have been processed and their properties were compared with those of neat EVA. First of all, in order to avoid the SNCs destructuration or gelatinization during the processing, EVA pellets and SNCs powder were dried for 24 hours under vacuum at 35 °C. EVA/SNCs nanocomposites were obtained by a microextruder equipped with twin conical corotating screws (MiniLab Haake Rheomex CTW5, Thermo Scientific) with a capacity of 7 cm³. A screw rotation rate of 75 rpm, temperature of 120°C, and residence time of 4 min were used. The processed nanocomposites were named EVA-2SNC and EVA-

5SNC highlighting the SNCs amount into the EVA matrix. The extruded nanocomposites were successively thermo-compressed in a Dr. Collin 200mm x 200mm press at 120°C and 50 bars in order to obtain films to carry out their characterization.

2.4 Characterization Techniques

The thermal properties were investigated by Differential Scanning Calorimetry (DSC) analysis. The dynamic DSC measurements were performed in a Mettler Toledo DSC822e instrument, under nitrogen flow (30 ml/min). Samples of about 10 mg were sealed in aluminum pans. Thermal cycles were composed by the following “heat/cool/heat” procedure: heating at 10 °C min⁻¹ from -80 °C to 150 °C, cooling at 10 °C min⁻¹ to -80 °C and heating again at 10 °C min⁻¹ to 150 °C. The first scan was done to erase prior thermal history of the samples. From second and third scans, the crystallization temperature (T_c), glass transition temperature (T_g), melting temperature (T_m) and the melting enthalpy (ΔH_m) were obtained. Glass transition temperatures were determined at the inflection point. The degree of crystallinity (X_c) of each sample was calculated, according with the equation below:

$$X_c (\%) = \frac{\Delta H_m}{\Delta H_m^{100}} \times 100 \quad (1)$$

where, ΔH_m^{100} is the specific melting enthalpy for a 100 % crystalline PE (293 J/g) as considering that VA comonomer units are not able to participate in the crystalline lattice (Brogly, Nardin, & Schultz, 1997).

Dynamic Mechanical Thermal Analysis (DMTA) of the samples was carried out using a DMA Q800 from TA Instrument in film tension mode with an amplitude of 5 μm, a frequency of 1 Hz, a force track of 125 %, and a heating rate of 2 °C·min⁻¹. Samples

subjected to DMA were cut from compression-molded thin films into regular specimens of approximately 20 mm × 5 mm × 0.60 mm.

Thermogravimetric analysis (TGA) was carried out using a TA-TGA Q500 thermal analyzer. Neat EVA and EVA/SNCs nanocomposites were analyzed by dynamic mode using about 10 milligrams of sample from room temperature to 800 °C at 10 °C min⁻¹ under nitrogen flow (60 mL min⁻¹). Temperatures at the maximum degradation rate (T_{max}) were calculated from the first derivative of the TGA curves (DTG).

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) measurements were carried out with a Spectrum One FTIR spectrometer (Perkin Elmer instruments). Spectra were obtained in transmission mode at room temperature in the 4000-650 cm⁻¹ region with a resolution of 4 cm⁻¹ and 32 scans.

X-ray Diffraction (XRD) measurements were performed using a Bruker D8 Advance instrument with a Cu K α source (0,154 nm) and a detector Vantec1. The scanning range was 4°-40°, step-size and count time per step were 0.023851° and 0.2 seconds, respectively.

The morphology of native WBS granules and SNCs were studied by Scanning Electron Microscopy (SEM PHILIPS XL30 with a tungsten filament). WBS and SNCs samples were dispersed in distilled water and ultrasonicated for 10 minutes. Then, a small droplet of the dilute suspension was deposited on glass sample holder and dried at room temperature. All the samples were gold/palladium coated by an automatic sputter coated Polaron SC7640. Field Emission Scanning Electron Microscope (FE-SEM, Hitachi S8000) in transmission mode was used to observe SNCs morphology as well as their dispersion into the EVA matrix in the nanocomposites. SNCs were dispersed in distilled water and ultrasonicated for 10 minutes. Then, a small droplet of the dilute suspension was deposited on a copper grid and dried at room temperature. The nanocomposite

films were cut into ultra-thin sections with a microtome for FE-SEM observation. SNCs morphology was observed also with Transmission electron microscope (TEM) using a Philips CM200 electron microscope, using an accelerator of 120 kV.

Atomic force microscopy (AFM) experiments were performed in tapping mode, TM-AFM, using a Multimode AFM (Veeco Instruments, Santa Barbara, CA) equipped with a Nanoscope Iva control system (software version 6.14r1). Silicon tapping probes (RTESP, Veeco) were used with a resonance frequency of ~300 kHz and a scan rate of 1 Hz.

Mechanical properties were determined using an Instron Universal Testing Machine at a strain rate of 150 mm min⁻¹ in order to avoid the strain hardening effect of EVA. Tensile test measurements were performed on 5 dog-bone specimens with a width of 2 mm, thickness of 0.60 mm and leaving an initial length between the clamps of 20 mm. From these experiments were obtained the Young Modulus, as the slope of the curve between 0 % and 2 % of deformation, the elongation at break and the maximum stress reached.

3. Results and Discussion

SEM micrograph of native WBS granules suspension in water is reported in Figure 1.a. WBS granules showed a lenticular-like shape with a diameter of around 15-20 μm and homogeneous size distribution, in agreement with the literature (Fredriksson, Silverio, Andersson, Eliasson, & Åman, 1998). In general, starches are categorized in three crystalline types called A, B and C (T. L. Wang, Bogracheva, & Hedley, 1998) depending on their X-ray diffraction pattern. The differences in the crystalline structure could render different nanocrystals morphology (LeCorre, Bras, & Dufresne, 2011). A-type structure is frequently distinguished by strong reflections at $2\theta = 15.11^\circ$, 17.14° , 18.14° and 26.27° , with some additional reflections at $2\theta = 9.98^\circ$, 11.19° , 22.93° , 23.68° ,

30.30° and 33.08° (Lopez-Rubio, Flanagan, Gilbert, & Gidley, 2008; Mutungi, Passauer, Onyango, Jaros, & Rohm, 2012). X-ray patterns of WBS granules and the obtained SNCs (WBSNC), are shown in Figure 1.b. Acid hydrolysis treatment effectively led to remove the amorphous domains of starch granules while leaving the crystalline part intact. Indeed, X-ray patterns of native WBS as well as of WBSNCs display all the characteristic peaks of the A-type structure ($2\theta = 9.9^\circ, 11.2^\circ, 15^\circ, 17.1^\circ, 17.9^\circ, 19.8^\circ, 22.9^\circ, 26.4^\circ, 30.3^\circ$) according with their morphology. In Figure 1.c and 1.d, the SEM and TEM micrographs of SNCs are reported, respectively. SNCs tended to self-aggregate after lyophilization but they preserve the same shape and homogeneous size distribution. They present a length of 35-50 nm and a width of 15-25 nm, in good agreement with the literature (Yixiang et al., 2014).

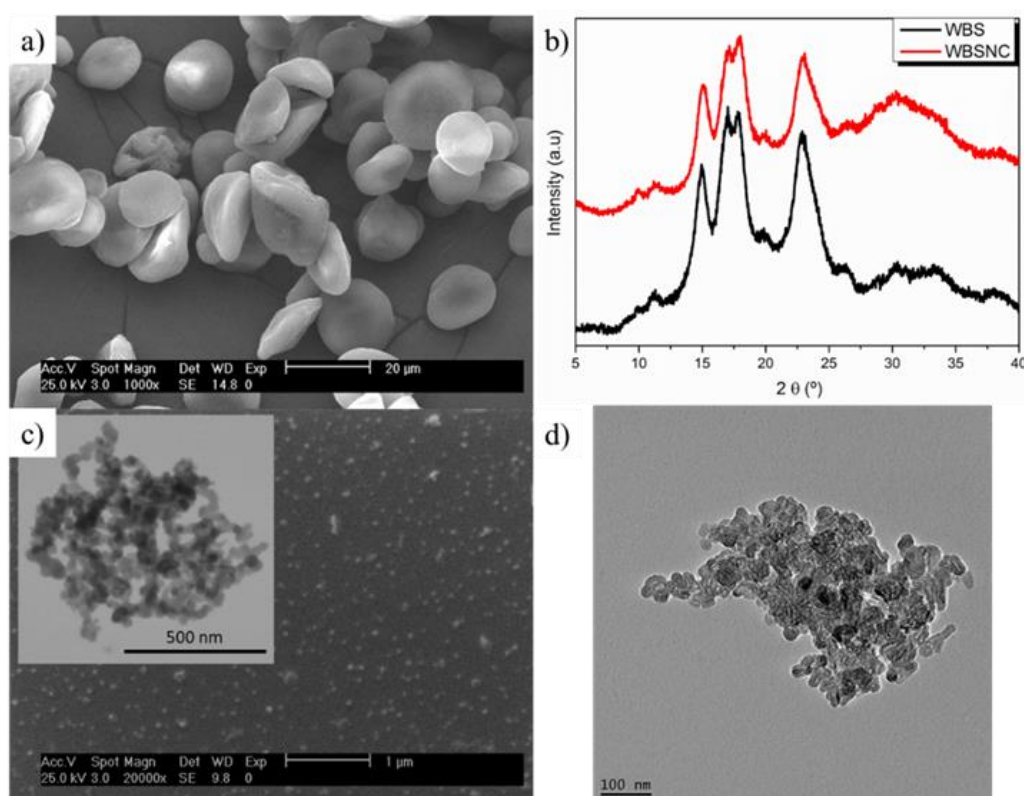


Figure 1. Morphology and crystalline structure of WBS and SNCs. a) SEM micrograph of native WBS granules, b) X-ray patterns of WBS and WBSNC, c) SEM and FE-SEM (inset) micrographs of WBSNC and d) TEM micrograph of WBSNC.

It is well known that the reinforcement effect of nanofillers depends on such factors as its dispersion into the polymeric matrix (Y. Wang et al., 2010) and their interfacial interaction with the polymeric matrix (Chauve et al., 2005; Peponi et al., 2014).

At this regard, in order to study their interfacial interaction, ATR-FTIR spectra of the EVA/SNCs nanocomposites, SNCs and neat EVA are shown in Figure 2. The ATR-FTIR spectra of neat EVA and its nanocomposites show the typical bands of vinyl acetate at 1737, 1238 and 1020 cm^{-1} and those of ethylene at 2917, 2850, 1464, 1371 and 719 cm^{-1} . These bands are in good agreement with the literature values (Bidsorkhi et al., 2015; Khodkar & Ebrahimi, 2011).

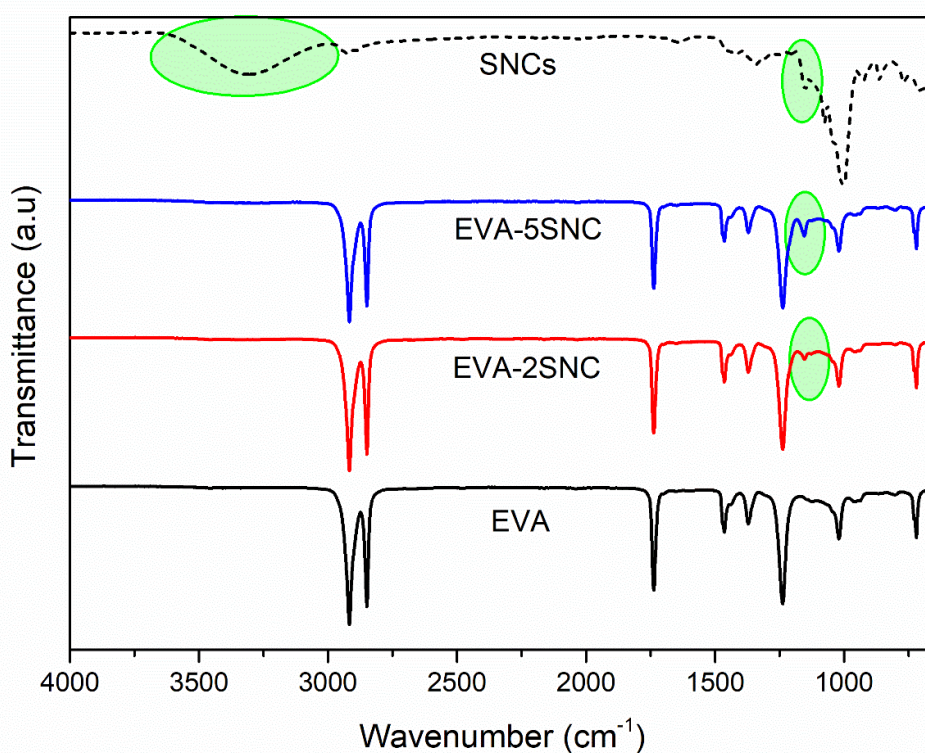


Figure 2. Full ATR-FTIR spectra of SNCs, neat EVA and EVA/SNCs nanocomposites.

The bands at 2917 cm^{-1} and 2850 cm^{-1} in the spectra of EVA samples have been attributed to the asymmetric and symmetric vibrations of aliphatic groups $(-\text{CH}_2)_n$, respectively. The 1737 cm^{-1} band corresponds to carbonyl stretching vibrations of the

acetate groups. Furthermore, the spectrum of SNCs shows the typical bands of starch. The O-H stretching mode of starch was observed in the region of 3000 and 3600 cm^{-1} and the C-H stretching modes in the 2800-3000 cm^{-1} region. The band observed at 1642 cm^{-1} was attributed to the O-H bending of absorbed water in the SNCs. The stretching vibration of C-O bond in C-O-H and C-O-C group in the anhydrous glucose ring appeared at 1150, 1075, and 1005 cm^{-1} . Meanwhile, the shoulder absorption at 1045 cm^{-1} was associated with the crystalline phase of SNCs as reported in literature (Gong et al., 2016). Finally, the characteristic band of C-O-C ring vibration of starch was observed at 769 cm^{-1} (Kizil, Irudayaraj, & Seetharaman, 2002). The addition of SNCs into the EVA matrix enhances the intensity of the band at 1150 cm^{-1} compared to neat EVA spectrum. Moreover, increasing the amount of SNCs, in the EVA/SNCs nanocomposites spectra, this band appears shifted at higher values from 1150 cm^{-1} to 1153 and 1155 cm^{-1} for EVA-2SNC and EVA-5SNC, respectively. Simultaneously the intensity of the O-H stretching band of SNCs observed in the region of 3000 and 3600 cm^{-1} was almost absent for both EVA-2SNC and EVA-5SNC. The changes observed in the spectra of EVA/SNCs nanocomposites suggested the possible presence of hydrogen bonding interactions between SNCs and EVA matrix. Similar results were previously reported for EVA/halloysite and poly(vinyl alcohol)/SNCs nanocomposites (Bidsorkhi et al., 2015; Chen et al., 2008).

The physical interaction between EVA and SNCs was reflected also in the dispersion of the fillers into the polymer matrix that was studied by FE-SEM in transmission mode. The FE-SEM images at different magnification are shown in Figure 3.

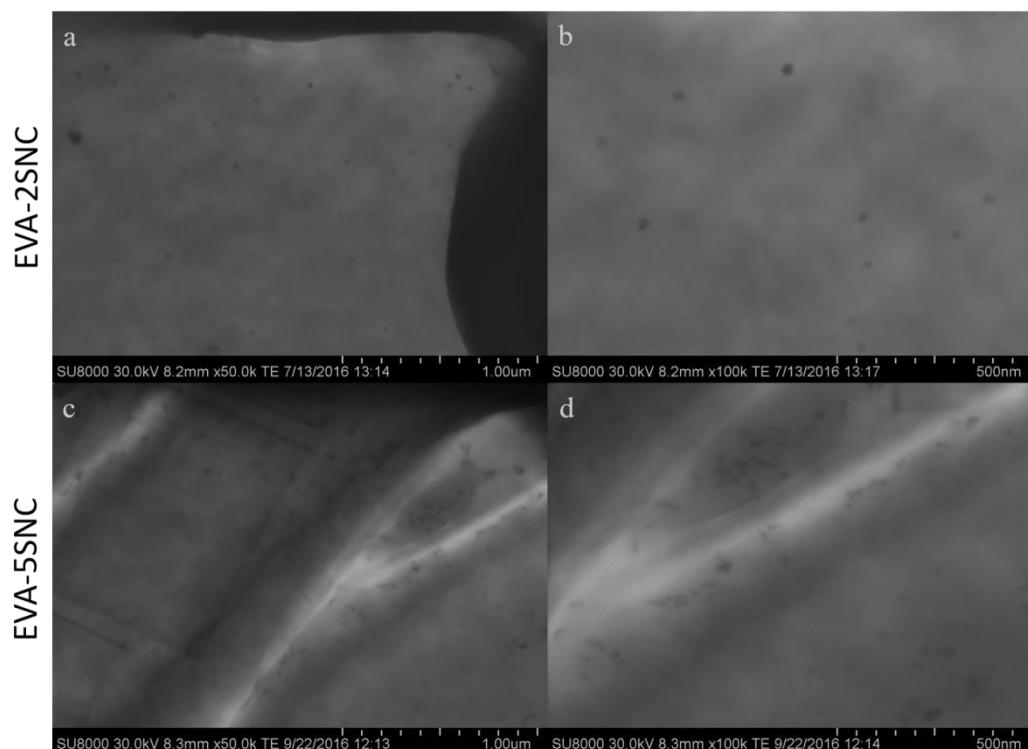


Figure 3. FE-SEM images at different magnification of a) EVA-2SNC at 50000x, b) EVA-2SNC at 100000x, c) EVA-5SNC at 50000x and d) EVA-5SNC at 100000x.

The FE-SEM images showed quite good dispersion of the SNCs in both nanocomposites confirming that during the melt processing, the SNCs were not destructured by maintaining their structural dimensions. The homogeneous dispersion of the SNCs in the EVA matrix depends on the interaction between the SNCs and the polar group of EVA, resulting in a good adhesion on the interfaces of SNCs and EVA matrix as it was previously demonstrated for poly (vinyl alcohol)/SNCs nanocomposites obtained by solvent casting (Chen et al., 2008). To further verify the presence of crystalline SNCs into the polymeric matrix, XRD measurements were performed and reported in Figure 4.

A thermal treatment has been done on SNCs in order to simulate the thermal processing conditions used to obtain the nanocomposites, submitting them at 120 °C for 3 min, naming them SNCs TT in Figure 4.a. Then, the XRD of SNCs has been performed

showing that the crystalline structure of SNCs was kept even after the thermal treatment.

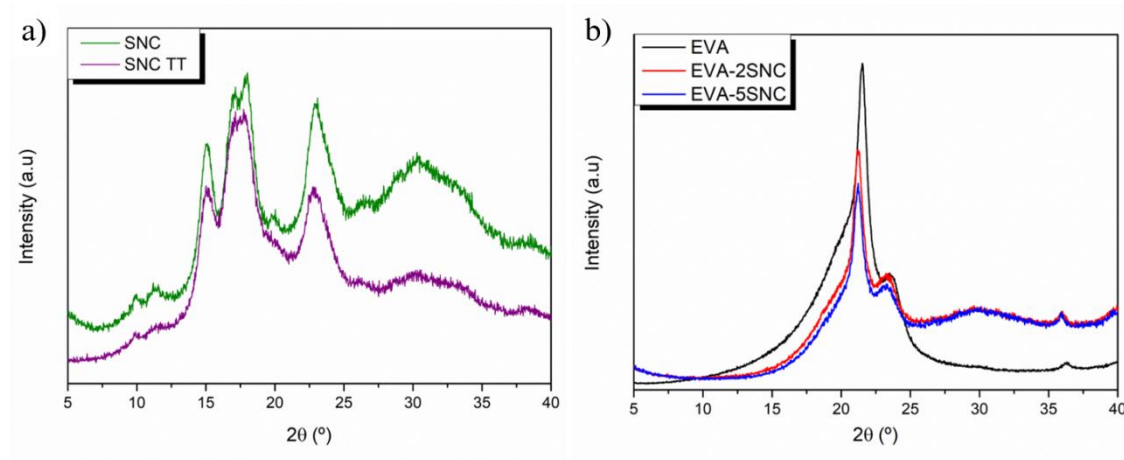


Figure 4. XRD patterns of a) neat and annealed SNCs and b) neat EVA and its nanocomposites.

As reported in Figure 4.a, X-ray patterns of SNCs display all the characteristic peaks of the A-type structure ($2\theta = 9.9^\circ$, 11.4° , a strong intensity peak at 15.1° , a double peak at 17.1° and 17.9° and a last strong intensity peak at 23.1°) with a broad peak at around $2\theta = 30.3^\circ$. The thermal treatment did not change the crystalline structure of the SNCs.

Figure 4.b indicates XRD patterns of neat EVA and its nanocomposites. Neat EVA showed an X-ray pattern with strong and broad crystalline peak at $2\theta = 21.5^\circ$, resulting mainly from the crystalline region of EVA due to polyethylene crystals as it was previously reported in literature. The X-ray pattern of EVA-2SNC and EVA-5SNC show the typical peak of EVA at $2\theta = 21.5^\circ$ and the broad peak of SNCs at $2\theta = 30.3^\circ$. However, the other typical diffraction peaks of SNCs were shielded by the diffuse diffraction of EVA matrix.

TM-AFM images, Figure 5 and Figure 6, have been also performed in order to study both the morphology and the dispersion of SNCs after their processing. In particular, in

Figure 5, 10x10 μm TM-AFM height and phase images are reported for EVA-2SNC, while in Figure 6, 3x3 μm TM-AFM height and phase images are reported for EVA-5SNC. The inset of both figures represent the sections of SNCs.

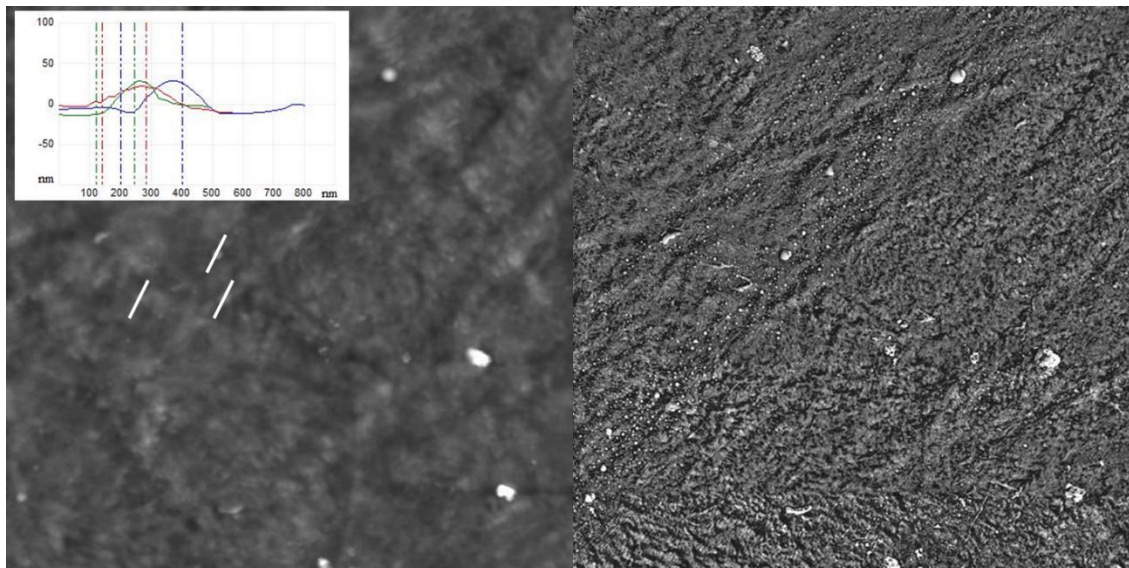


Figure 5. 10x10 μm TM-AFM height and phase images for EVA-2SNC.

In Figure 5, thanks to the 10x10 μm images, it is easy to note the good dispersion of the SNC in the EVA matrix, where no agglomeration are reported, in good agreement with previous results obtained from the previous FE-SEM analysis. Moreover, as indicated in the inset of the figure, the sections of the SNCs are reported in order to study their dimension after the processing. It is worth to note that no change on the dimension of the SNCs are reported, being their dimension comparable with the neat ones.

At difference of EVA-2SNC, nanocomposite obtained with 5 wt.% of SNCs presented small agglomerations, as indicated in Figure 6. Even in this case, it is easy to note that the dimension and the morphology of the SNCs are not changed after the processing conditions when the nanocomposites are obtained. However, as expected, the small agglomerations found in the EVA-5SNCs can affect the mechanical performance of the nanocomposites.

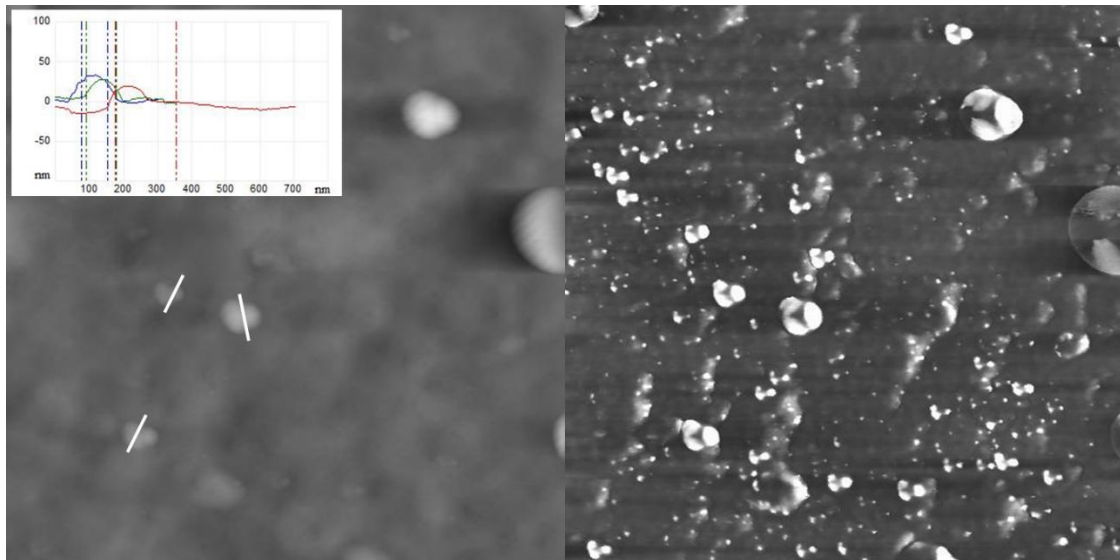


Figure 6. 3x3 μ m TM-AFM height and phase images for EVA-5SNC.

The strong hydrogen bonding between the SNCs and the acetate groups of EVA lead to the improvement of the mechanical and thermal properties of the neat matrix. Tensile test of neat EVA and its nanocomposites were performed. The stress-strain curves are reported in Figure 7.a.

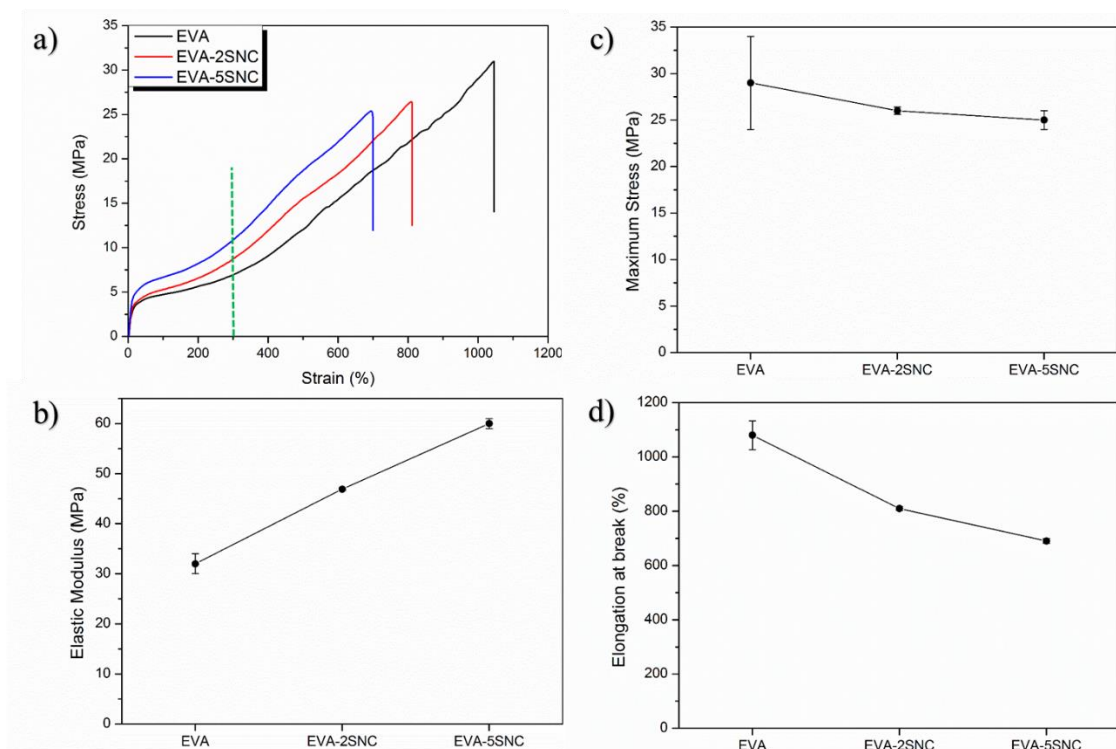


Figure 7. a) Stress-strain curves of neat EVA and its nanocomposite. Trend of mechanical properties as a function of SNCs content. b) Elastic Modulus, c) Maximum Stress and d) Elongation at break.

Neat EVA shows the typical stress-strain curve of rubber polymers, characterized by high elongation at break and low elastic modulus. Strain hardening it was observed in all the samples due to the chain orientation in the stretching direction, leading to high stress at break (Ray, Khastgir, & Mukunda, 1993). The mechanical properties of neat EVA and EVA/SNCs nanocomposites are listed in Table 1.

Table 1. Mechanical properties of neat EVA and its nanocomposites

Sample	Elastic Modulus (MPa)	Maximum Stress (MPa)	Elongation at break (%)	Stress at 300 % (MPa)	Modulus at 300 % (MPa)
EVA	32 ± 2	29 ± 5	1080 ± 53	6.96 ± 0.53	1.45 ± 0.48
EVA-2SNC	47 ± 1	26 ± 1	810 ± 7	8.73 ± 0.05	2.96 ± 0.09
EVA-5SNC	60 ± 1	25 ± 1	690 ± 9	10.96 ± 0.14	3.53 ± 0.08

The mechanical properties were significantly affected by the addition of SNCs. With increasing the amount of SNCs in the nanocomposites, the elastic modulus increased as compared with that of neat EVA. In particular, when 5 wt.% of SNCs has been added to EVA, a double elastic modulus has been obtained. However, the maximum stress was quite constant and the elongation at break decreased with the addition of SNCs, probably due to the small agglomerations obtained when 5 wt.% SNCs are added to EVA matrix. However, comparing our results with those of Pereda et al. (Pereda et al., 2014) for LDPE-based nanocomposites reinforced with unmodified starch nanocrystals processed by melt-processing, it is possible to notice that in our case the mechanical properties were still improved at 5 wt.% of nanocrystals.

In Figure 7, the trend of mechanical properties as a function of SNCs content is shown. The modulus of the different samples was calculated at 300 % of strain as well in order to study the effect of SNCs addition on the mechanical properties before the strain hardening of the matrix (Table 1). It is worth to note that the moduli at 300 % of strain become higher with SNCs content in the EVA matrix, showing increases of around 100 % and 140 % for EVA-2SNC and EVA-5SNC, respectively. Moreover, the same trend was observed for the stress at 300 % of strain, differently from the values of the maximum stress recorded. In fact, it was found that in EVA-2SNC and EVA-5SNC the stress at 300 % show increases of 25 % and 58 %, respectively. However, a small

variation has been observed at higher strain level (>300 % strain) where the modulus of pure EVA becomes slightly higher than those of its nanocomposites. It was observed that the nanocomposites undergo strain hardening at lower elongation percentages compared with neat EVA. This phenomenon might be attributed to the orientation of the crystalline polyethylene segments present in EVA, as reported in literature (Ray et al., 1993; Varghese, Bhagawan, Rao, & Thomas, 1995). In case of EVA-2SNC and EVA-5SNC as the amount of SNCs increased, the degree of crystallinity increased and the mobility of the polymer chains was restricted, leading to lower values of elongation at break and maximum stress as compared with neat EVA. Thus, the decrease of the strain at break of the EVA/SNC nanocomposites was directly related with crystallinity increase as shown in Table 2, where the DSC results are reported.

A T_g at around -26 °C was observed for neat EVA and it was related to the amorphous phase, consisting of amorphous PE and amorphous VA segments as previously reported in literature (Nöchel et al., 2014; Reding, Faucher, & Whitman, 1962). No changes were observed in the T_g values for the nanocomposites with respect to neat EVA. The results in terms of T_g , T_m , T_c , ΔH_m , ΔH_c and X_c are summarized on Table 2.

Table 2. Thermal properties and degree of crystallinity.

Samples	T_c (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)	T_g (°C)
EVA	70	86	53	18	-26
EVA-2SNC	71	87	69	24	-26
EVA-5SNC	71	87	73	25	-26

Neat EVA had a T_m of 86 °C and a T_c of about 70 °C. No variations in melting and crystallization temperatures were observed by DSC analyses, while an increase of

enthalpy of fusion upon incorporation of SNCs is reported in Table 2. These results suggest that the increase of SNCs content improved the degree of crystallinity of EVA matrix likely due to the nucleation effect of the SNCs. Similar results were showed by Zou et al. (Zou et al., 2011), obtaining higher values of ΔH_m for waterborne polyurethanes/SNCs nanocomposites compared with that of the neat polymer thanks to the nucleation effect of SNCs. The same phenomenon was reported by Viguié et al. (Viguié, Molina-Boisseau, & Dufresne, 2007) for thermoplastic starch nanocomposites reinforced with SNCs.

The dynamic mechanical properties of neat EVA and its EVA/SNCs nanocomposites were studied by DMA technique. The storage modulus (E'), the loss modulus (E'') and dumping factor ($\tan \delta$) as a function of temperature are shown in Figure 8. The peak temperatures in Figure 8.b and 8.c are referred to the alpha-transition (glass transition) of EVA.

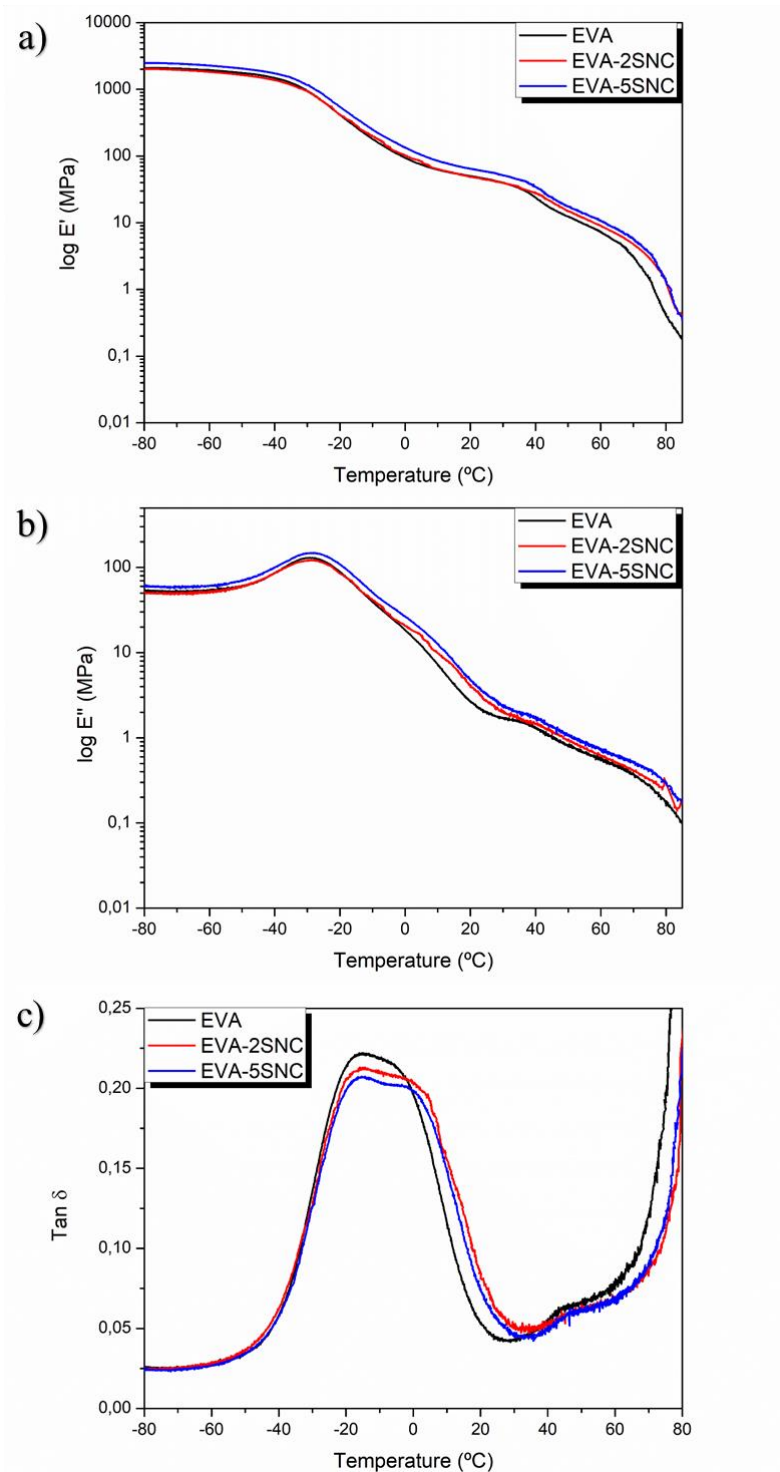


Figure 8. Dynamic mechanical properties: a) storage modulus (E'), b) loss modulus (E'') and c) damping factor ($\tan \delta$) of neat EVA and EVA/SNCs nanocomposites as a function of temperature.

At low temperature, below T_g , the storage modulus underwent a slight enhancement with respect to the neat matrix upon addition of the nanoparticles. This behavior was expected as reported in literature for elastomeric matrices reinforced with SNCs (Haaj et al., 2014; Y. Wang et al., 2010) and it is attributed to the relative low difference between the modulus of the glassy matrix and that of the nanofiller network, considering the low filler amount. Thus, neat EVA in the glass state showed relatively high E' values (~ 2000 MPa) that increased by 500 MPa after addition of 5 wt.% of SNCs. No significant changes were observed after the addition of 2 wt.% of SNCs. Similar results were observed in waterborne polyurethane/SNCs systems as well (Zou et al., 2011). The slight enhancement of the storage modulus, as the result of the filler addition, was observed also in the rubbery region, indicating the presence of EVA-SNCs interfacial interactions. This leads to a slight delay on the drop of the E' curve corresponding to the melting of PE crystals. Moreover, the peak width of $\tan\delta$ increased adding SNCs, indicating higher internal friction caused by EVA-SNCs interaction. Similar results were reported for EVA/CNC nanocomposites, where the interfacial interaction between CNCs and EVA matrix was confirmed by the increase of the intensity and peak width corresponding to the T_g of EVA (Ma, Jiang, Hoch, Dong, & Chen, 2015).

Finally, the thermal stability of the EVA/SNCs nanocomposites was studied by thermogravimetric analysis conducted under dynamic mode. Figure 9 shows the TGA and its derivate (DTG) curves of the nanocomposite films as well as of neat EVA under nitrogen atmosphere. Thermal degradation of EVA takes place in two steps as it was previously reported in literature (Zanetti et al., 2001). In the first stage, deacylation with the elimination of acetic acid and the formation of double bonds occurs in the range of

270-380 °C. At temperatures higher than 380 °C, thermal degradation of the ethylene-co-acetylene random copolymer resulting from deacylation takes place.

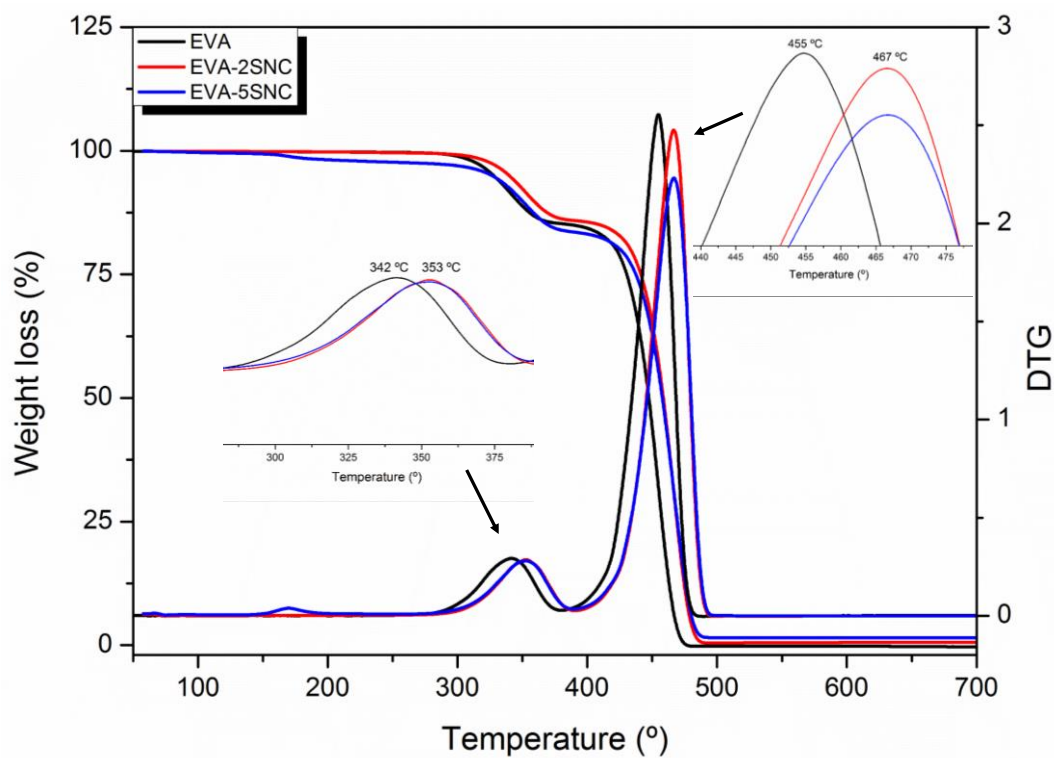


Figure 9. TGA and DTG curves of neat EVA and its nanocomposites.

The weight loss curves of the nanocomposites (Figure 9) display a slight stabilization of about 10 °C, thus SNCs did not change the nature of degradation, but alters the temperature for maximum degradation. EVA-2SNC showed the initial degradation temperature ($T_{5\%}$) at 340 °C, EVA-5SNC showed it at 326 °C while neat EVA showed its $T_{5\%}$ at about 328 °C. The first maximum degradation temperature ($T_{\max I}$) was about 353 °C for both EVA-2SNC and EVA-5SNC whereas $T_{\max I}$ for neat EVA was about 342 °C. Finally, the second maximum degradation temperature ($T_{\max II}$) was about 467 °C for both the EVA-SNCs nanocomposites, while neat EVA had its $T_{\max II}$ at about 455 °C as it is showed in Figure 9. Furthermore, a reduction of almost 2 wt.% was observed at 170 °C, corresponding to the degradation temperature of SNCs. The improvement in thermal stability was attributed to the homogeneous dispersion of SNCs, originated

from the interaction between the hydroxyl groups on the SNCs surface and acetate groups of EVA. The increase on the thermal stability thanks to the interaction between EVA and nanofillers was already reported in literature, *i.e.* for EVA/Halloysite nanotubes nanocomposites (Bidsorkhi et al., 2015) and EVA/sepiolite nanocomposites (Bidsorkhi et al., 2014). Furthermore, the thermal stabilizing effect of SNCs due to the strong interaction between the OH-group on the SNCs surface and the polymer matrix was already reported for, *i.e.*, waterborne polyurethane/SNCs nanocomposites (Y. Wang et al., 2010) and in starch/SNCs nanocomposites (Li et al., 2015).

4. Conclusions

Green nanocomposites based on EVA and SNCs were successfully prepared by extrusion without lose their crystalline nature. DSC analysis showed the increase of the degree of crystallinity when higher amount of SNCs were loaded into the EVA matrix. The different changes in the FTIR spectra of EVA/SNCs nanocomposites compared to that of neat EVA were attributed to the positive interactions between the vinyl acetate groups of the matrix and the hydroxyl groups of SNCs. These physical interactions were reflected in the good and homogeneous dispersion of the nanofillers into the polymer matrix and on the enhanced mechanical properties of the nanocomposites. Indeed, adding 2 wt.% and 5 wt.% of SNCs into the EVA matrix, the elastic modulus increases around 50 % and 100 % respectively, comparing with the neat matrix, without variation on the maximum stress. Moreover, thermal stability of the prepared nanocomposites was improved of about 10 °C by the incorporation of up to 2 wt.% of SNCs. This work provided important information about the possibility to introduce SNCs in a polymeric matrix by melt-processing and about their use to improve EVA performances thanks to hydrogen bonding interaction between the matrix and the fillers.

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