CHARACTERIZATION OF ETHYLENE-VINYL ACETATE (EVA) USED IN ORTHOPEDIC INSOLES

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RESUMEN

Las órtesis son parte de la inmensa industria de dispositivos médicos cuyo objetivo es mejorar la vida del paciente, mediante la corrección o el tratamiento de lesiones. Por lo tanto, es de gran importancia comprender las propiedades físicas, químicas y mecánicas de los materiales utilizados para desarrollar estos productos. Esta investigación utiliza las técnicas de difracción de rayos-X, análisis de termogravimetría y calorimetría diferencial de barrido, espectroscopía infrarroja por transformada de Fourier y microscopía electrónica de barrido, para la caracterización del etilvinilacetato (EVA) utilizado en Costa Rica para la fabricación de plantillas ortopédicas. Dichas técnicas permitieron identificar características específicas de dos muestras de EVA con distinto valor de dureza en la escala Shore, tales como la presencia de carbonato de calcio ($CaCO_3$), la cantidad de acetato de vinilo presente en el compuesto, una temperatura de fusión de 72° C y diferencias en la densidad del material. Los resultados mostraron que la razón principal en la variación de dureza entre ambas muestras es la cantidad de acetato de vinilo presente, la cual se puede aumentar o disminuir según requisitos específicos.

ABSTRACT

Orthotics are part of the immense medical devices industry; their aim is to improve the patient's life by correcting or treating injuries. Therefore, it is of great importance to understand the physical, chemical and mechanical properties of the materials used to develop these products. This research uses techniques such as X-ray diffraction, thermogravimetric and differential scanning calorimetry analyses, Fourier transform infrared spectroscopy and scanning electron microscopy, for the characterization of ethylene-vinyl acetate (EVA) used for manufacturing orthopedic insoles in Costa Rica. These techniques allowed to identify specific characteristics of two EVA samples with different value of hardness in the Shore scale, such as the presence of calcium carbonate ($CaCO_3$), the amount of vinyl acetate in the compound, a melting temperature of 72° C, and differences between the material's densities. The results show that the main reason in the variation of hardness between both samples is the amount of vinyl acetate present which can be increased or reduced according to specific requirements.

PALABRAS CLAVE

Acetato de etileno-vinilo, acetato de vinilo, ortopedia, dispositivo médico, plantillas ortopédicas.

KEYWORDS

Ethylene-vinyl acetate, vinyl acetate, orthotics, medical device, orthopedic insoles.

INTRODUCTION

Feet are structures subject to high levels of biomechanical stress and impact due to their overuse in activities of daily life or sports; therefore, the presence of dysfunctions in musculoskeletal or neuronal structures are common; this stress and impact can cause pain and even disability [1,2].

The use of orthotics as means of correction and treatment of injuries caused by abnormal structures or foot joint dysfunction is a common practice. This orthotics must resist abnormal foot pressure; aiming to correct and restore normal alignment of the lower extremities, in order to promote proper foot support on uneven and unstable surfaces [3].

Currently, there are different hardness levels for this polymer (according to the Shore hardness scale) used in the manufacturing processes of these medical devices. Hardness level are personalized depending on the clinical needs of the patient; therefore, it is of great interest to determine what compounds in the molecular structure of the material modify the polymer properties by increasing or decreasing its hardness.

This study allowed to characterize Ethylene-Vinyl Acetate (EVA) using different methods. X-ray diffraction (XRD) has its origin in the elastic dispersion of the X-ray beam that passes through the atoms of the sample, where the electrons of the material disperse the wave at the same angle of incidence (θ-Theta), hence this radiation emerges at an angle 2θ with respect to the direction of the incident beam, conserving its initial energy. This type of diffraction is described by the Bragg Law which predicts in what direction a constructive interference occurs between the electromagnetic waves dispersed in a crystal [4].

Thermogravimetric Analysis (TGA) is a method of thermal examination where changes in the chemical and physical properties of the material are measured in relation to changes in temperature (or isothermal as a function of time). This information allows the study of phenomena such as: decomposition of the material, phase transitions, desolvation and solid-gas reactions. It is possible to detect such reactions if there is change in mass related to the change in temperature [5]. Differential scanning calorimetry (DSC) is another thermoanalytical technique where the heat difference needed to increase the sample temperature and that of a reference material is measured as a function of temperature [6].

Fourier Transform Infrared spectroscopy (FTIR) is a vibrational spectroscopic technique used to obtain a spectrum on a large variety of simultaneous wave elements, creating a spectrum that collects separate signals at each wave number [5]. This thermal energy radiation (low-energy electromagnetic waves) induces molecular vibrations in covalent bonds, which can vibrate in different ways, including symmetrical and asymmetrical stretching, swinging, scissor, flutter and twist vibrations. This technique can provide information about the functional groups of an unknown molecule. It is a widely-used method for performing measurements, quality control and dynamic measurements. It also allows to measure the degree of polymerization in the manufacturing of polymers [5].

Scanning Electron Microscopy (SEM) analysis, is a technique in which images are produced from a sample that is scanned by a focused beam of electrons. These electrons interact with the atoms of the sample producing secondary and backscattered electrons, as well as characteristic X-rays, which are quantified by different detectors and produce information about the topology and chemical composition of the sample [5].

The main limitations of the study revolve around the difficulty of performing repetitive tests on the polymer samples, so the results obtained are unique and are not comparable with other results from the same sample. It is understood that EVA is a composite polymer but the molecular structure and chemical composition is unknown, making it difficult to relate the results obtained with the production sheet of the material where it was synthesized.

Understanding the physical, chemical and mechanical properties of the material used for the construction of 3D printed insoles is essential to ensure success in therapy. Through the analysis of elemental composition in the molecular structure, this work intends to characterize the EVA material, which is used for manufacturing orthopedic insoles in Costa Rica, by means of the aforementioned techniques.

MATERIALS AND METHODS

X-Ray Diffraction Analysis (XRD)

In order to obtain the chemical compounds or phases present in the crystalline structure of EVA polymer, an X-ray diffraction analysis was conducted. The samples were pulverized EVA material of 50 shore hardness (EVA 1) and pulverized EVA of 25 shore hardness (EVA 2), with a PANalytical Empyrean diffractometer, located at the School of Materials Science and Engineering, Costa Rica Institute of Technology. This diffractometer used a radiation source of copper (Cu-K_α) powered with 40 mA and 45 KV. The analysis was carried out at room temperature with a scanning range from 10° to 80° (2θ), step size of 0.0130° (2θ) and a scan step time of 3.57 s.

Thermogravimetric Analysis (TGA)

This test was performed at the National Nanotechnology Laboratory (LANOTEC-CeNAT) with the TGA Q500 from TA Instruments, under at ultra-high-purity nitrogen atmosphere, with a balance gas of 10.0 ml/min and sample gas of 90.0 ml/min. The temperature ramp used in this technique was at 20° C/min from 30° C to 500° C, at this point, the ramp was increased to 50° C/min up to 1000° C. The air cool time was 25.0 min.

Differential Scanning Calorimetry (DSC)

The experiment was performed at the National Nanotechnology Laboratory (LANOTEC-CeNAT), using the DSC Q200 from TA Instruments. It was possible to obtain information about the purity of the EVA samples, transitions of state (fusion and glass transition, among others), and the effect of stabilizers and pressure [5]. The temperature range used for this analysis was from 25° C to 150° C, with a 20° C/min ramp in an inert atmosphere of ultra-high-purity nitrogen (50.0 ml/min). This atmosphere was also used as a reference material during the experiment.

Fourier Transform Infrared Spectroscopy (FT-IR)

The ThermoScientific Nicolet 6700 FT-IR with the ATR (Attenuated Total Reflectance) sampling accessory, located at the National Nanotechnology Laboratory (LANOTEC-CeNAT), was used on a small sample of the material pressed on top of the diamond crystal. A total of 32 scans were averaged, provided the necessary information for this analysis from the pattern library in the equipment.

Scanning Electron Microscopy (SEM)

This test was performed at the Institutional Microscopy Laboratory, Costa Rica Institute of Technology, using a HITACHI TM-1000 microscope. A Denton Vacuum Desk IV ion coater was used to coat the sample in a gold-palladium conductive layer to allow the conductance of electrons in the surface, given that EVA is not conducting material.

RESULTS

XRD Analysis

Table 1 and 2 show the results of XRD analysis for peaks of the EVA 1 and EVA 2 samples, respectively. The tables show the position angle, peak height, peak width at half maximum (FWHM), atomic d-spacing and the relative intensity of each sample peak. Analysis of the EVA 1 and EVA 2 samples by XRD allowed the indexation of their diffraction spectra, with a match to Ethylene-Vinyl Acetate polymer spectrum of the equipment data library, as shown in Figure 1. The most significant difference between the spectra corresponds to the position of the highest intensity peak, where for EVA 1 it is in the crystallographic plane (100) (2θ=21.3980°) and for EVA 2 in (210) (2θ=29.5299°). Table 3 shows the positions (2θ) of the Ethylene-Vinyl Acetate polymer spectrum, its interplanar distances and the respective Miller Indices. There was also a match for calcium carbonate ($CaCO_3$) in both samples. The peaks for this substance are close to the EVA reflections at 29.3905°, 39.3997° and 48.4891°, corresponding to the (104), (113) and (116) planes.

Table 1. *Results of the EVA 1 XRD analysis.*

POS. (°2 Th.)	HEIGHT (cts)	FWHM LEFT (°2 Th.)	D-SPACING (Å)	REL. INT. (%)
21. 3980	1192.67	0.3838	4.15264	100.00
23.5461	227.43	0.3070	3.77844	19.07
26.5812	58.13	0.2047	3.35350	4.87
29.4120	830.26	0.2558	3.03687	69.61
31.4852	26.81	0.4093	2.84147	2.25

Table 2. *Results of the EVA 2 XRD analysis.*

POS. (°2 Th.)	HEIGHT (cts)	FWHM LEFT (°2 Th.)	D-SPACING (Å)	REL. INT. (%)
21.4520	150.33	0.5117	4.14232	45.65
23.2129	51.14	08187	3.83191	15.53
27.5578	44.67	0.2047	3.23684	13.56
29.5299	329.32	0.1791	3.02501	100.00
36.2522	74.76	0.3070	2.47803	22.70

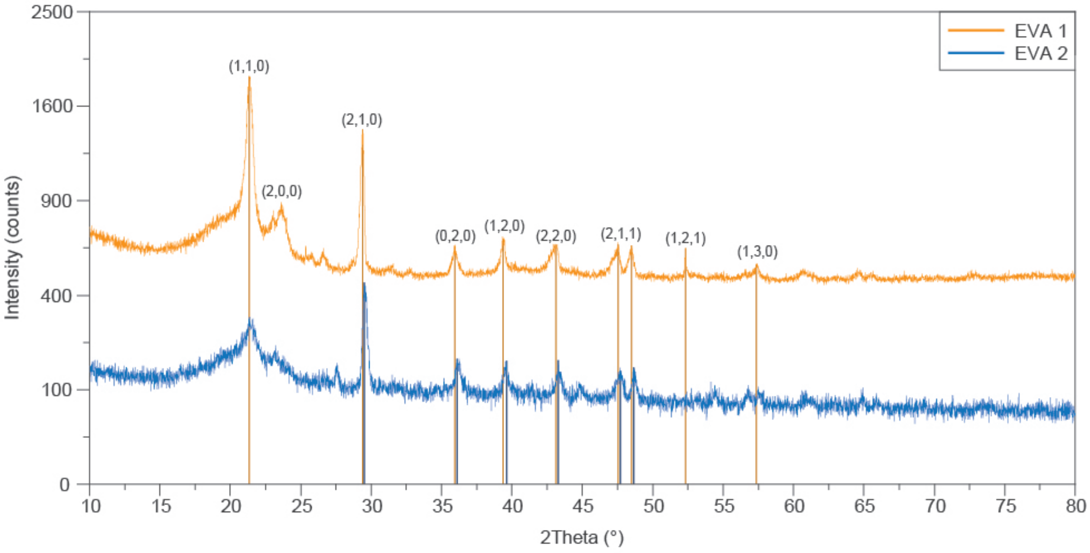


Figure 1. *Comparative XRD graph of EVA samples.*

Table 3. X-Ray Diffractometry Reference for EVA Polymer.

POS. (°2 Th.)	D-SPACING (Å)	I	h	k	l
21.4826	4.132970	999	1	1	0
23.7245	3.747230	197	2	0	0
29.8714	2.988650	9	2	1	0
36.2333	2.477160	36	0	2	0
38.2342	2.352000	14	1	2	0

TG Analysis

Figure 2 shows the comparative chart of the TG analyses corresponding to the EVA 1 and EVA 2 samples, respectively. This type of analysis provided the amount of vinyl acetate present in a copolymer such as Ethylene-Vinyl Acetate. The results of both samples show decomposition at temperatures between 393 °C and 496 °C. In addition, both samples display a decomposition curve in several stages with no stable intervals. These results agree with the literature for the decomposition pattern of vinyl acetate, which occurs in the first stage (350-400 °C). The amount of vinyl acetate for EVA 1 corresponds to 12.43% and for EVA 2 to 26.83%.

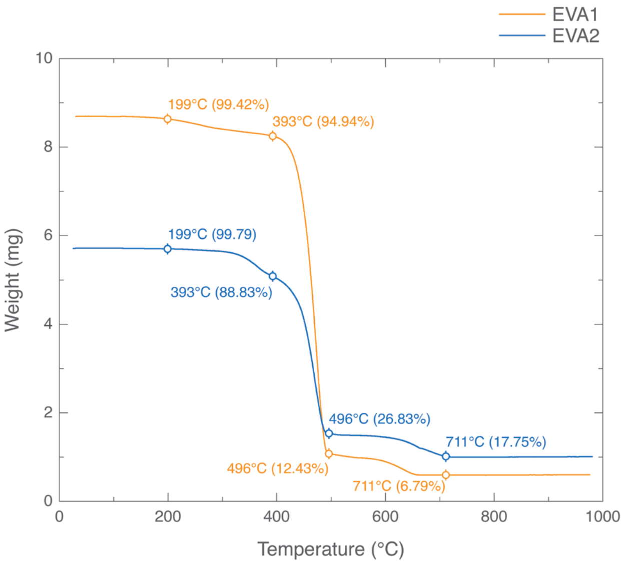


Figure 2. Comparative TGA graph of EVA samples.

DSC Analysis

Figure 3 shows the DSC curves of the EVA 1 and EVA 2 samples respectively, obtained with a heating ramp of 20° C/min from room temperature up to 150° C. The most intense peak in the EVA 1 sample occurs at a temperature around 116° C and corresponds to an endothermic fusion in the compound (starting at about 70° C). This corresponds to the onset for melting of the Ethylene-Vinyl Acetate copolymer. EVA 2 presents changes of enthalpy before 80° C, however, there is no defined peak as in EVA 1.

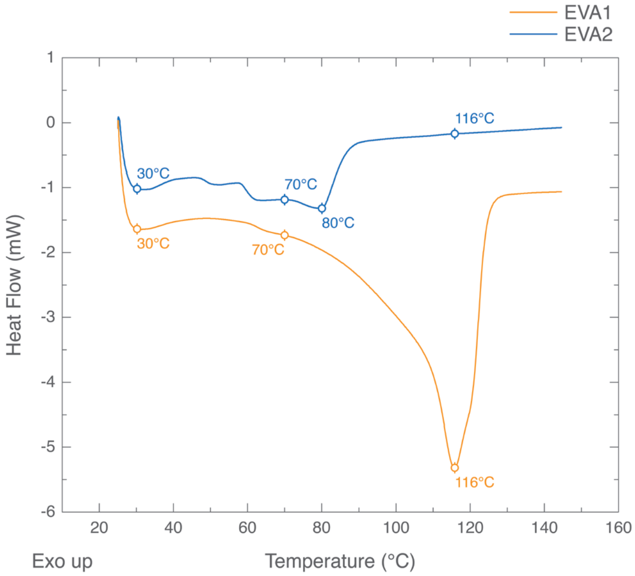


Figure 3. Comparative DSC plot of EVA samples.

FTIR Analysis

According to Figure 4, it is notorious that the main differences occur between 2000 cm^{-1} and 1500 cm^{-1}, where two notable peaks are detected in the EVA 2 sample. These peaks are due to the detection of the extremely polar covalent bonds of the compounds. Peaks located between 3000 cm^{-1} and 2750 cm^{-1} show a strong polar covalent bond corresponding to bonds between C-H and O-H. In addition, a peak of medium polar intensity can be observed in the EVA 2 sample near 1750 cm^{-1}, which corresponds to the double bonds of C-C and C-O.

It is also important to mention that the "fingerprint" zone (between 1400 cm^{-1} and 600 cm^{-1}) of the graph shows a peak of medium intensity and 2 peaks of low intensity in the EVA 2 sample, corresponding to the single bonds between C-C and C-O, respectively, while for EVA 1 only a medium intensity peak and several almost undetectable peaks were found.

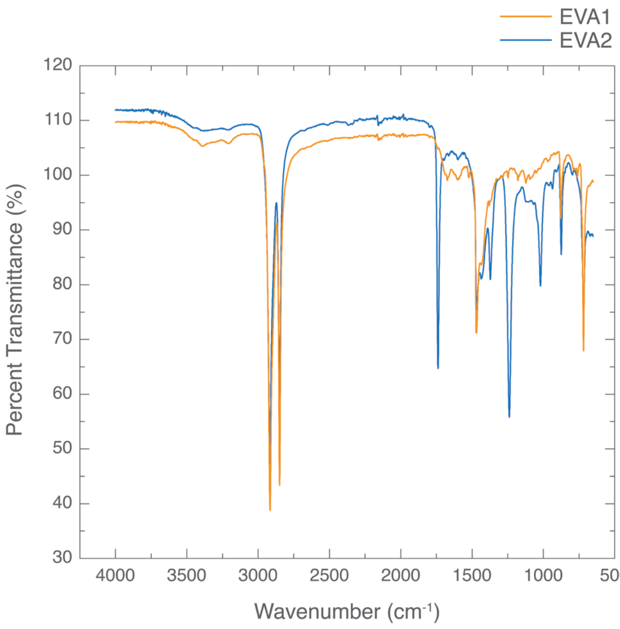
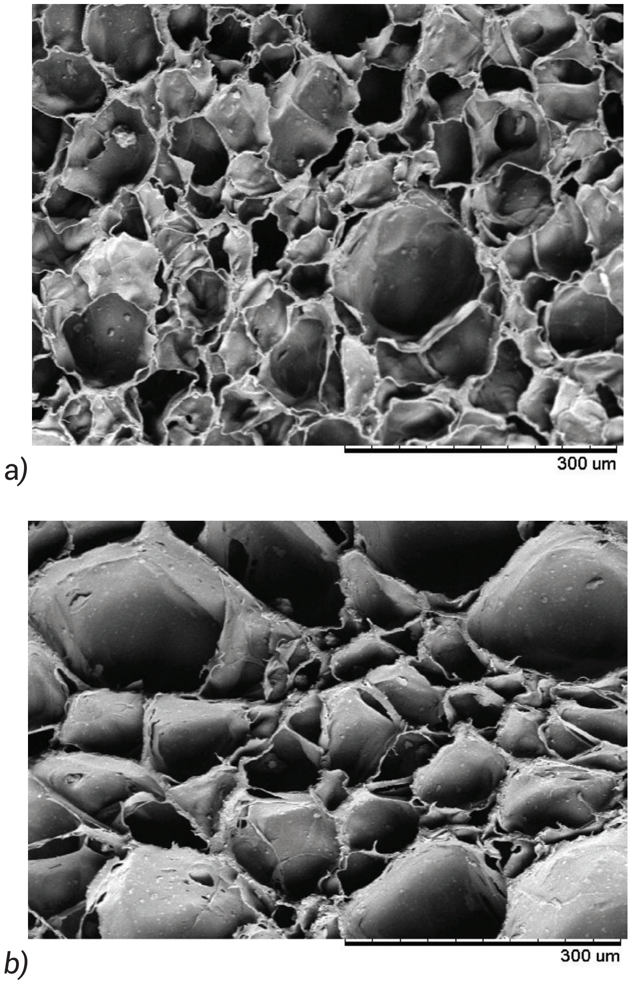


Figure 4. *Comparative FTIR graph of EVA samples.*

SEM Analysis

The images in Figure 5a and 5b correspond to scanning electron micrographs of the EVA 1 and EVA 2 samples, respectively, with a scale corresponding to a magnification of 250x.



a)

b)

Figure 5. *SEM micrographs of both EVA samples. a) EVA 1 and b) EVA 2.*

Using the linear intercept method, the cell size was obtained for both samples. The procedure followed for the calculations can be seen in Figure 6. Horizontal and vertical lines were drawn onto the micrographs, and the total number of intersections of the lines with cell borders were count. For the EVA 1 sample, the total horizontal length was 17.85 µm, with 385 intersections for an average cell size of 46.4 µm. In the vertical axis, the total length was 17.60 µm, with 419 intersections for an average 42.0 µm. For the EVA 2 sample, the total intercepts in the horizontal direction were 282, for an average cell size of 63.3 µm. Vertically, the total number of intercepts was 335, resulting in an average cell size of 52.5 µm. The aspect ratio of the cells was then 1.1 and 1.2 for the EVA1 and EVA2 samples respectively, which can be considered equiaxed.

A reduction of 27% of the cell size was seen in the horizontal direction, and of 19% in the vertical axis, from EVA 2 with respect to EVA 1.

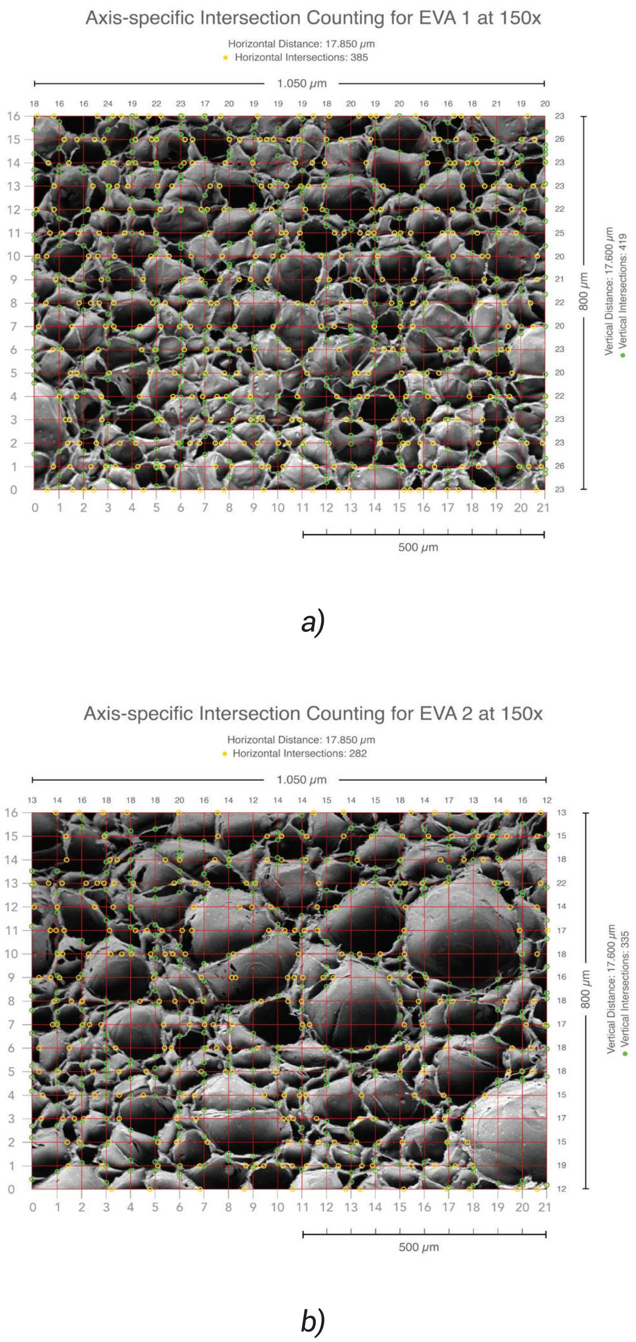


Figure 6. *Lineal intercept method for EVA samples at 150x. a) EVA 1 and b) EVA 2.*

DISCUSSION

The XRD analysis identified $CaCO_3$ as a component of the sample. $CaCO_3$ has been used in the industry of orthopedic medical devices; being part of the formulation of bone cements for bone repair, prosthesis manufacturing and as a component of controlled drug release systems [7]. Additionally, literature reports that this compound has been used for the improvement of the mechanical resistance of materials [8], for this reason it can be inferred that it was added to the orthopedic insoles formula. It is important to underline that the component is present in both samples tested and the test does not provide information of concentration, therefore it is not possible to confirm that $CaCO_3$ is the responsible for the different levels of hardness of the material.

The most significant difference between the EVA diffraction in the EVA 1 and EVA 2 samples was the intensity of the emission, being stronger the (110) plane in EVA 1; which is affected by the collective scattering of all the atoms in the crystal, but it does not represent a significant difference between the samples. The structure of EVA detected corresponds to a cubic crystalline structure [9].

The TGA analysis showed a process with decomposition temperatures equal to the ones reported in the literature for Ethylene-Vinyl Acetate, and occurs in two phases. The first one is at approximately 350° C and corresponds to the loss of acetic acid; which is 20% of the vinyl acetate weight. This compound is reported to have a direct impact on the mechanical behavior of the polymer, being typically used to increase the flexibility of the materials [10]. In the second mass change, around 500-650° C, the acetic acid has been totally lost and the polymer backbone is decomposed releasing hydrocarbons.

The melting temperature of EVA was determined with DSC test as 72° C, which seems to correspond to the EVA 2 sample, since EVA 1 seems to have a much higher melting temperature. Because of this it can be concluded that EVA 1 is thermally more stable than EVA 2. However, is necessary to perform additional tests to determine the reason for these differences.

Using the FT-IR analysis it was determined that both samples have strongly polar covalent bonds, corresponding to C-H bonds; in addition, EVA 2 sample has a medium polar intensity peak near to 1750 cm^{-1}, which corresponds to the acetic acid bond. The FT-IR test had the limitation that the fingerprint zone was not compared to a database, therefore an integral analysis of the results that reveals other possible compound(s) in the samples is not available.

The SEM analysis allowed to observe the microstructure of the insoles and recognize the cellular structure. This structure can be achieved in the orthotics industry by adding a blowing agent to the Ethylene-Vinyl Acetate preparation, then heat is applied causing the blowing agent to evaporate and leave bubbles through the material.

The results obtained with the lineal intercept method previously discussed suggests that EVA 1 has the smaller cell size of both samples, providing evidence that, either the blowing agent was different for each sample or, that the blowing agent time was shorter for EVA 1 than for EVA 2. The uniformity of the size of the cells can be inferred from the SEM images. Comparing Figure 5a with Figure 5b, one can see that EVA 1 has more uniformity of cell sizes. These are important features to analyze since it can affect the properties of the material, therefore contributing to the differences of Shore hardness and thermal stability.

CONCLUSIONS

The results showed that the main compound present in the samples corresponds to Ethylene-Vinyl Acetate. Through XRD and TGA characterization techniques, it can be inferred that a higher presence of the vinyl acetate polymer (acetic acid + ethylene) increases the flexibility of the material, however it decreases the crystallinity of Ethylene-Vinyl Acetate.

Results obtained from TGA also determined that in the first decomposition of EVA 2, it lost more mass than EVA 1 under the same circumstances. Thus, according to the literature, EVA 2 has a higher concentration of vinyl acetate in its formulation than EVA 1.

Different Shore hardness between EVA 1 and EVA 2 may be affected by the size and uniformity of the cells of its structure. It was determined that the smaller and more uniform cell size was of EVA 1, corresponding to the highest Shore hardness. The concentration of $CaCO_3$ could also contribute to the hardness levels.

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