Influence of Calcium Carbonate Concentration on the Properties of Polypropylene Stretched Flat Tapes Used in Raffia Packaging

Joyce Batista Azevedo[1*], Benjamin Lazarus[2], Rosindo Pereira Lobo Junior[1], Willams Teles Barbosa[1], Luã Fonseca Seixas[1], Josiane Dantas Viana Barbosa[1]

[1]SENAI CIMATEC University Center; Salvador, Bahia, Brazil; [2]University of California; Materials Science and Engineering Program, San Diego, California, USA; [3]Federal University of Bahia; Institute of Science, Technology and Innovation, Camaçari, Bahia, Brazil

The production of stretched polypropylene (PP) tapes for packaging has recently led to advancements in raffia packaging, which has improved multiple technical characteristics. In addition to the beneficial economic impact, this packaging is more sustainable. The present work evaluated the properties of stretch tapes obtained with different concentrations of calcium carbonate ($CaCO_3$) to reduce the cost of production of raffia packaging. We produced the tapes in an industrial environment using a single-screw extruder with a flat die containing 3, 7, 10, 15, 17, and 20 wt % of $CaCO_3$. The tensile strength, elongation, and toughness of the tapes were evaluated. Tensile strength and toughness increase with the addition of $CaCO_3$ while the elongation decreases. Stearic acid ($CH_3(CH_2)16COOH$) in the filler contributed positively to the dispersion and distribution of the filler in the matrix, preserving the mechanical properties. The results showed that incorporating $CaCO_3$ in flat strips stretched from PP emerges as an alternative for cost reduction with raw material for raffia packaging.
Keywords: Polypropylene. Calcium Carbonate. Raffia. Stretched Tapes.

Introduction

In the 1980s, woven sacks made of natural fibers such as cotton or jute were the most widespread solutions in the packaging market for grain, sugar, seeds, and many other agricultural products. However, with the emergence of synthetic fibers called raffia, sack production began to transition away from these natural fibers. Thus, the packaging market saw the emergence of an economically more attractive alternative with characteristics of resistance, durability, and reuse [1].

Synthetic raffia packaging comprises several stretched tapes, and its manufacturing process consists of polymeric materials extrusion. Polypropylene (PP) and polyethylene (PE) are generally used in a single-screw extruder with a flat die. This process involves the extrusion of flat films and the cutting and drawing of the tapes. Initially, films are produced in a flat die extruder [2-4]. In this step, it is essential to control the crystallization of the polymer [5].

This work used an isotactic homopolymer PP with ~50%-80% crystallinity [6]. This property can be adjusted during production by changing the distance between the surface of the cooled water bath and the matrix, as well as the temperature of the bath water. These operational parameters directly interfere with the polymer crystallization process, defining the size and quantity of spherulites that form. Furthermore, the degree of crystallinity directly affects the tensile strength and elongation of the tapes [7].

After obtaining the film, it is cut into tapes. A cylinder with special blades and spacers pulls the film in tension for this operation. After cutting it, the ribbons are subjected to stretching [8]. The stretch is performed at different peripheral speeds between groups of cylinders positioned in sequence. It promotes the stretching of the raffia, resulting in a decrease in its width. This process is necessary to define the tape's final width and achieve the physical properties necessary for the optimal performance of the final product. However, as it is a physical and not a rheological process, stretching

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Address for correspondence: Joyce Batista Azevedo. Avenida Orlando Gomes, 1845, Piatã. Salvador, Bahia, Brazil. Zipcode: 41650-010. E-mail: joyce.azevedo@ufba.br.

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has limitations in the amount of stretching applied. It can negatively affect the product's mechanical properties if applied in excess or outside of pre-existing working standards used in the industry [8,9].

The stretching process creates a plastic deformation forcing the movement of the amorphous phase chains, as well as the reorientation of the crystals of the crystalline phase, increasing the mechanical strength due to the high orientation of the structures [10-12]. Therefore, it is necessary to apply a thermal treatment in the oriented film to avoid many problems in the process and the product, such as lousy formation and loss of raffia rolls, increase in production residue, rupture, and decrease of the nominal load capacity of the packages, in this case, the already stretched raffia. Therefore, the stretched tape goes through a heating process in cylinders with temperatures between 110ºC and 120 ºC for PP tapes. The temperature range must consider the temperature used during the stretching process. It must be lower to allow a partial relaxation of the oriented tape, generating a shrinkage that usually varies from 5% to 10%. Consequently, oriented raffia does not present relevant shrinkage problems in use or further processes. The main physical properties desired for raffia are tensile strength and elongation, which can vary depending on the degree of stretching to which it is subjected [13].

Raffia produced with PP and other polyolefins has significant advantages over natural fibers such as jute, cotton, and sisal [4], despite its difficulty to be recycled. It does not rot, is chemically resistant, lightweight, water resistant, and easy to handle. However, because of the growth in industrial production, there is also a necessity to improve the quality of the product and reduce manufacturing costs.

One of the alternatives for reducing manufacturing costs and improving the mechanical properties of the tapes is incorporating calcium carbonate ($CaCO_3$) as a filler. Its cost is ~20% lower than the virgin raw material used in raffia production [14]. Therefore, this study aims to evaluate the incorporation of different concentrations of $CaCO_3$ in the PP matrix. For this, $CaCO_3$ was treated with stearic acid ($CH_3(CH_2)16COOH$) to increase its degree of hydrophobicity. Since $CaCO_3$ is a polar substance with a high specific surface, it is incompatible with PP, which is non-polar, thus impairing its dispersion in the matrix [15]. Several studies have shown that when the mineral filler is surface treated with compounds such as fatty acids, silanes, or polymers, there is an improvement in the compatibility between the phases, minimizing the polar nature of the mineral filler [16-18]. The production of synthetic raffia is a topic that has received little attention in scientific literature. Therefore, there is a knowledge gap with countless possibilities for studies in the processing and fabrication of this product, as well as the raw material used, which can improve the production and mechanical properties of the tape. In this context, this study examines fillers' influence on PP tapes' properties as an avenue for cost reduction. It also provides an evaluation of process conditions and properties.

Materials and Methods

Materials

The tapes were obtained from stretched flat films using the PP homopolymer H503 HS manufactured by Braskem S.A. (Brazil). This polymer has a fluidity index of 3.5 g/10min and a density of 0.905 g/cm³ [6].

The $CaCO_3$ (80 wt %) used is a natural ground calcite with low plasticizer absorption, treated with 1.2 % stearic acid and granulometry ranging from 2.2 - 12 μm, supplied by Micron-Ita Ltda. (Brazil). The choice of the type of $CaCO_3$ is due to the greater ease of incorporation into mixtures because of its surface treatment with stearic acid.

Stretched Tapes

The PP tapes were manufactured with a Star EX 1600 flat die extruder by Star-linger Group (Austria), with a capacity of 650 kg/h and a

final winding speed of up to 550 m/min. Table 1 describes the processing conditions. Concentrations of 3, 7, 10, 15, 17, and 20 w/w % of Ca-CO_3 were added to the PP matrix to obtain the tapes. For each formulation, 6 samples were obtained with a width of 4.9 mm and a thickness of 27.1 μm.

Characterizations

The selection of characterization techniques used in this work considers the mechanical stresses of tapes when used to produce sack-type packages.

The characterizations were performed according to BS 4611:1989, which defines test methods for polyolefin tapes [19]. Thus, in the tapes produced with $CaCO_3$, the tensile strength, elongation, and tenacity were determined. The results were compared to that presented by a PP tape without added carbonate provided by Group CATA Nordeste (Brazil). In addition, the fluidity index (IF) of the compounds was determined, and differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) were performed to complement the mechanical characterization and elucidate the crystallinity and morphology of the PP tapes with and without the $CaCO_3$ filler.

Mechanical Properties

The mechanical evaluation of the tapes was carried out through an analysis of tensile strength, elongation, and tenacity. These tests were performed on a universal machine Emic model DL3000 in the test laboratory of the Group CATA, using a gripper distance of 250 mm and a constant speed of 250 mm/min. The test was performed on 6 samples of each composition. The samples were stored at a controlled temperature (25 °C) and humidity (55 %).

Fluidity Index (FI)

The FI analysis was performed using a DSM MI-1 plastometer, according to ASTM D-1238 [20], with a temperature of 230 °C, a load of 2.16 kg, a waiting time between samples of 20 seconds, and a material stabilization time of 100 seconds. In addition, the samples were dried for 3 hours at 100 ºC in an oven before the test.

Table 1. Process conditions for obtaining the strips stretched with $CaCO_3$ in a flat die extruder.

Parameter	Value
Feed zone temperature	55 °C
Temperature of heating zones (Z1-Z8)	245; 255; 265; 270; 270; 275; 275; 275 °C
Filter temperature	275 °C
Matrix temperature	275 °C
Temperature in the drafting oven	180 °C
Bath water temperature	35 °C
Screw speed	67 rpm
Speed 1st to 5th stretch	107; 513; 500; 485; 475 m/min
Stretch rate	5.6
Tower cylinder pressure	4 a 5 Bar
Filter pressure	90 a 150 Bar
Speed 1st to 5th stretch	55 °C

Differential Scanning Calorimetry (DSC)

The DSC evaluation was performed using a Q100 Universal V4.3A (TA Instruments) at the Technology and Innovation Center of Braskem S.A. (Brazil). The test was performed on PP flat tape samples (raffia) with 10 % $CaCO_3$ before and after stretching over a temperature range of – 20 ºC to 200 ºC with a reference rate of 10 ºC/min. The objective of this test was to verify the effect of stretching on the crystallinity of the product.

Morphology

The morphology of the stretched tapes was analyzed using a Jeol JSM-6510 LV scanning electron microscope (SEM). In addition, the samples underwent a carbon deposition process on the surface using a Denton Vacuum Desk V model.

Results and Discussion

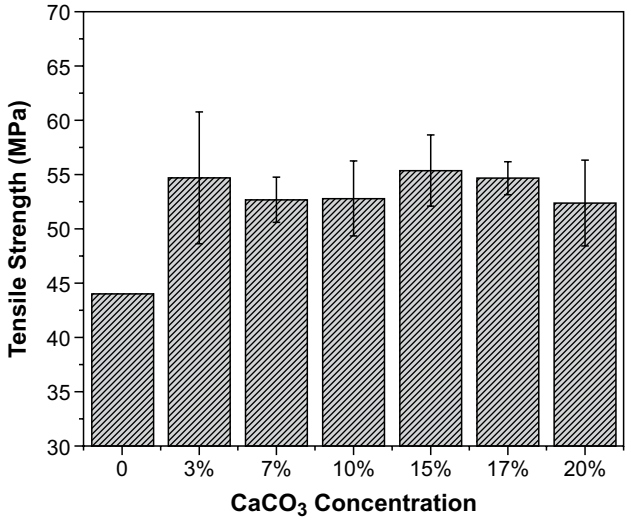
Figure 1 shows the tensile strength results of the tapes with and without the incorporation of $CaCO_3$. Tapes with $CaCO_3$ presented higher tensile strength than the tape without $CaCO_3$. The incorporation of the filler resulted in an increase in tensile strength between 16% and 19%. However, there was minimal variation in tensile strength with different concentrations of $CaCO_3$.

The mechanical behavior of polymers is closely related to their morphology. For example, in the stretching process, there is an orientation of the polymer chains, which results in the formation of crystals that increase the material's mechanical strength [10,21]. In this process, the molecular chains begin to orient in the stretching direction when the polymer is between its Tg (glass transition temperature) and Tm (crystalline melting temperature). Thus, the spherulites (polymeric crystalline structures) become anisotropic, and the highest applied stress is concentrated in the amorphous regions due to this alignment [22].

The molecular chains in the amorphous regions are randomly distributed, and because they are entangled, they can interact with multiple crystals simultaneously. Furthermore, the oriented molecules that connect to more than one crystal form a three-dimensional network since they form fixed bridges interconnecting the crystals, allowing for the uniformity of the flow of molecular chains during the stretching process, generating a film of constant thickness [22].

Adding solid particles to the semicrystalline polymer influences the molecular orientation process. The resultant toughening mechanism of this

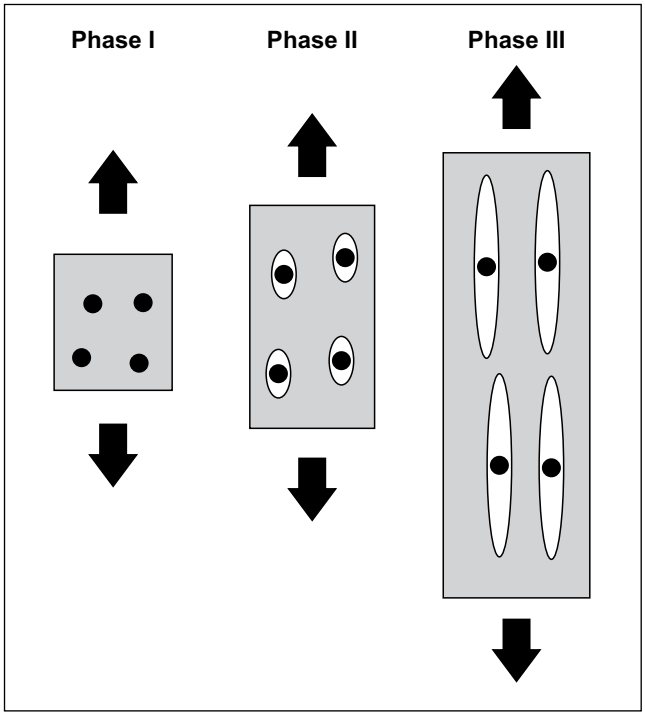
Figure 1. Tensile strength of tapes stretched with different concentrations of $CaCO_3$.



addition has been widely discussed in the literature. This mechanism involves changes in the polymer/charger interface, stress concentrations, and the formation of shear bands during loading [23-26].

Figure 2 shows a schematic of the debonding phenomenon that occurs during the stretching process of tapes that contain solid particles. At the beginning of the deformation, the filler acts as a stress concentrator in the matrix due to the difference between the elastic behavior of the phases (Phase I). As a result, a stress concentration is generated, and a triaxial stress state forms around the particle, referred to in the literature as delamination (Phase II). In the delamination phase, there is a displacement at the particle-polymer interface during flow. Finally, shear bands are created, leading to higher energy absorption during deformation (Phase III) [23,24].

Figure 2. Phases of the debonding phenomenon during the stretching process of tapes with the incorporation of solid particles.



Source: Adapted from Eirasa and colleagues and Zuiderduin and colleagues [23,24].

Figure 3 shows a micrograph of the surface of the stretched flat tape with 10 % $CaCO_3$ incorporation. We also observe that the debonding phenomenon (orange arrows) is possible.

As for the $CaCO_3$ content in the samples (Figure 1), there is no trend or significant variation in the results obtained for tensile strength. However, using a greater volume of filler without significant loss of mechanical properties implies a cost reduction and economic gain in manufacturing products made from the tapes.

Figure 4 presents the morphology of the extruded films before the stretching process. These scans verify that the surface treatment of stearic acid applied to $CaCO_3$ allowed the dispersion and homogeneous distribution of the matrix particles without forming agglomerates, which also benefits the material's tensile strength [17,18]. This behavior corroborates the results obtained for the fluidity index of the samples (Figure 5).

MFI results in Figure 5 presented a variation in the fluidity index between the sample. The highest values were obtained for the tapes with 10% $CaCO_3$ incorporation, compared to pure PP.

The flow index increased due to the mineral fillers behaving as a lubricant for the molten polymer. According to Guillet [26], viscosity reduction also occurs since, after treatment, the filler adsorbs the polymer more entirely and quickly due to the decrease in surface tension, increasing its dispersion and reducing the viscosity. Therefore, the filler particle size and surface treatment are required for the application studied. Since the mineral filler particle usually has a surface tension higher than the surface tension of the polymer. If there is no proper surface treatment, the particles tend to agglomerate and not disperse because the particle-particle interaction force can be greater than the particle-polymer force [18,24,27,28].Therefore, equalizing the surface tension of the $CaCO_3$ particles provided by the surface treatment may have contributed to better dispersion (reduced agglomerates) and increased polymer-particle interaction, with a substantial increase in the flow index.

Figure 6 shows the elongation results of the stretched tapes. The elongation tends to decrease

Figure 3. Micrograph of the tape strip stretched with 10% $CaCO_3$ showing delamination (debonding) occurred during the stretching process.

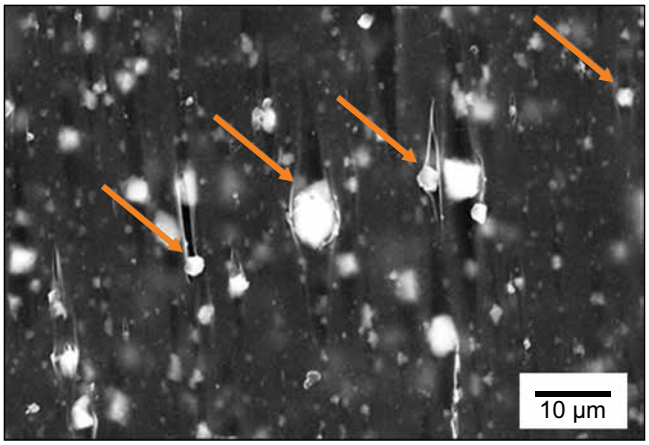


Figure 4. Micrographs of the surface of the flat tapes before stretching: (a) Tape with 10 % $CaCO_3$, and (b) Tape with 15% $CaCO_3$.

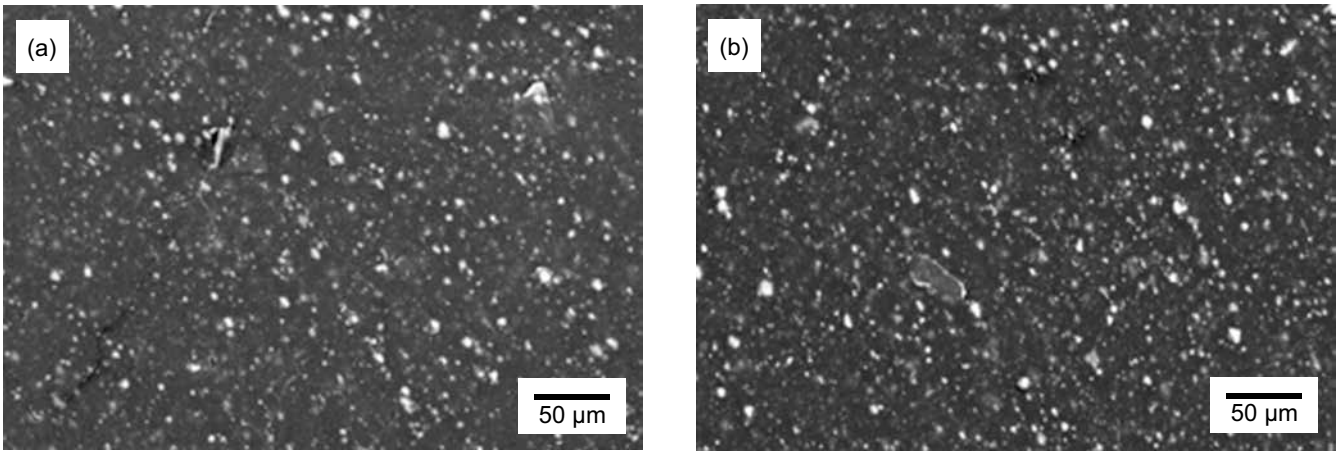


Figure 5. Melt flow index (MFI) of tapes stretched with different concentrations of $CaCO_3$.

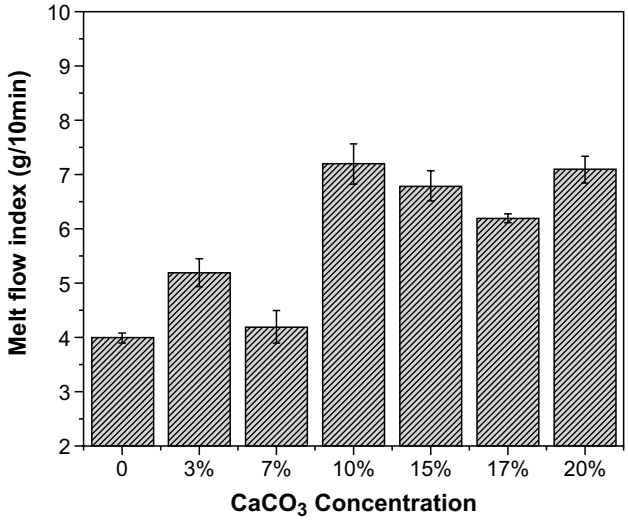
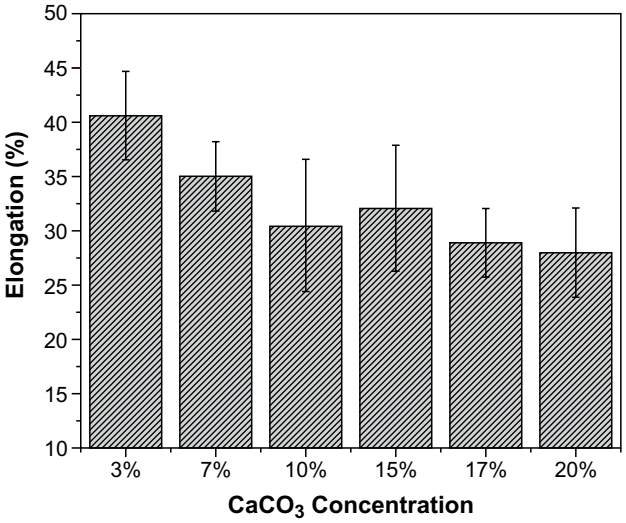


Figure 6. Elongation of stretched tapes.



with increasing concentrations of $CaCO_3$. The reduction in elongation may be related to the formation of agglomerates due to the higher concentration of $CaCO_3$ particles in the matrix, accentuating the delamination phenomenon. With the formation of agglomerates, there is an increase in fracture points, which reduces the elongation capacity of the tapes [24,29,30].

Another condition to consider is that the molecules in the amorphous region are very close when aligned, which can lead to stretch-induced crystallization during testing [22]. Ordered groups of molecules are formed, where the surface energy is similar to the energy of a crystal nucleus. Thus, a stretched film acquires a higher degree of crystallinity at the end of the orientation process [31].

Table 2 presents the results of the DSC analysis of the tapes with the incorporation of 10 % of $CaCO_3$ without styrel and after stretching. The crystalline melting temperature (Tm) and crystallization temperature (Tc) were close for both tapes. However, there was an increase in crystallinity for the tape after the stretching process, with a crystallization rate of 57.23 %, higher than the tape without stretching (54.05 %).

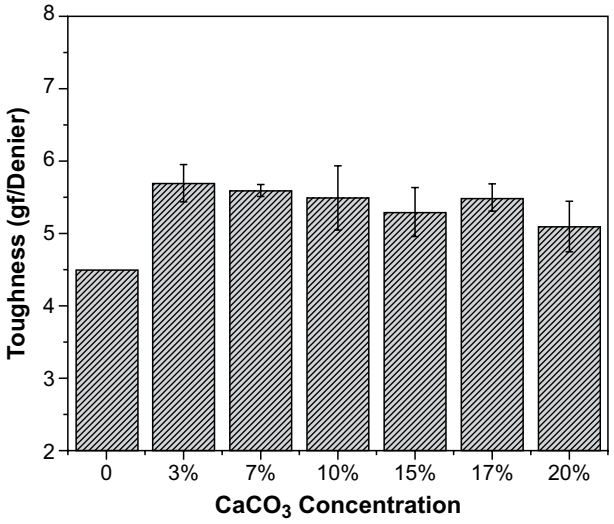
In an industrial scale process, it is also possible to control the degree of longitudinal alignment of the chains by keeping the tape stretching process under control. Consequently, the degree of crystallization can be controlled to guarantee that the final material has the desired tensile strength without sacrificing elongation [11]. This effect can be realized by controlling the film cooling steps before cutting the tapes, thus providing control over forced crystallization by cooling and/or controlling the stretch rate, forcing stretch-induced crystallization [13]. In addition, these process parameters can be controlled and worked individually or together during extrusion to obtain products with crystallization suitable to the required mechanical properties [7].

Figure 7 shows the toughness results for the stretched tapes. Again, there were no significant variations in the toughness of the tapes with the increase in the concentration of $CaCO_3$. However, the toughness values were higher than the minimum

Table 2. DSC analysis of tape with 10 % $CaCO_3$ before and after stretching.

Sample	TC (°C)	TM (°C)	Crystallization Rate
No stretching	118.12	163.73	54.05
After stretching	118.31	163.50	57.23

Figure 7. Toughness (gf/Denier) of the stretched tapes.



standard of 4.5 gf/Denier used by the raffia industry for this type of product [32].

During processing, there was an increase in dust generation during drawing as the concentration of $CaCO_3$ increased, most notably in concentrations above 15 %. It indicates that at high concentrations, the delamination phenomenon generated filler loss. It is important to emphasize that the addition of mineral filler to the polymeric matrix can lead to a reduction in the cost of the raw materials. It also brings improvement in some of the main mechanical properties of raffia.

Conclusions

It is possible to obtain flat-stretched PP raffia tape using $CaCO_3$ as a filler. The concentrations in this study did not alter the tensile strength and toughness properties considered standard for the raffia packaging industry. However, the elongation of the tapes was influenced by increasing the concentration of $CaCO_3$ and the crystallization obtained during the stretching of the tapes. Using $CaCO_3$ treated with stearic acid contributed to obtaining a better dispersion and distribution of the filler in the matrix, preserving the mechanical properties, and positioning itself as an alternative to reduce the cost of raw material for packaging with raffia.

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