

Processing and Properties of PCL/Cotton Linter Compounds

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Biodegradable compounds of poly(ϵ -caprolactone) (PCL)/ cotton linter were melting mixed with filling content ranging from 1% to 5% w/w. Cotton linter is an important byproduct of textile industry; in this work it was used in raw state and after acid hydrolysis. According to the results of torque rheometry no decaying of viscosity took place during compounding, evidencing absence of breaking down in molecular weight. The thermal stability increased by 20% as observed in HDT for PCL/cotton nanolinter compounds. Adding cotton linter to PCL didn't change its crystalline character as showed by XRD; however an increase in degree of crystallinity was observed by means of DSC. From mechanical tests in tension was observed an increase in ductility of PCL, and from mechanical tests in flexion an increase in elastic modulus upon addition of cotton linter, whereas impact strength presented lower values for PCL/cotton linter and PCL/cotton nanolinter compounds. SEM images showed that PCL presents plastic fracture and cotton linter has an interlacing fibril structure with high L/D ratio, which are in agreement with matrix/fibril morphology observed for PCL/cotton linter compounds. PCL/cotton linter compounds made in this work cost less than neat PCL matrix and presented improved properties making feasible its commercial use.

Keywords: Poly(ϵ -caprolactone) (PCL), cotton linter, compounds, processing, mechanical properties.

1. Introduction

Synthetic plastics have been used for various purposes, especially in the packaging, automotive, and health care industrial sectors. However, the majority of these materials constitute at present a serious waste management problem. Biodegradable polymers have attracted special attention as the plastics of the 21st century, since they can be biologically degraded and therefore can be considered as environmental friendly materials¹⁻³. Biodegradable polymers are by definition those that degrade as a result of the action of microorganisms and/or enzymes. They are a specific type of polymer that breaks down after its intended purpose to result in natural byproducts such as gases (CO₂, N₂), water, biomass and inorganic salts. These polymers are found both naturally and synthetically made^{4,6}.

PCL is a linear aliphatic semicrystalline polyester, synthesized by ring-opening polymerization of the cyclic lactone in presence of a catalyst. PCL is a polymer with good ductility because of its low glass transition temperature of -60°C. Due to its biodegradability, biocompatibility and

environmental friendliness PCL has been used for packaging, agriculture and medical devices, as well as a substitute of non-biodegradable commodity polymers⁷⁻⁹.

Cotton linter is a widely available, renewable, low cost, and biodegradable reinforcement. It is an important byproduct of the textile industry, composed of short fibers that cling to cottonseeds after the first ginning. The fuzzy seed needs to be subjected to an additional process that will mechanically remove the linter. The amount of linter produced worldwide is around 2.5 million metric tons, considering the 42 million metric tons of cotton lint produced in 2010. Traditional products made from linter are: absorbent cotton, special papers, cellulose nitrate, and acetate. In some cases, the linter is not extracted, but kept with the seed (when it is used for oil extraction) or chemically dissolved (for planting the seed)¹⁰⁻¹³.

PCL is a commercial polymer, fully biodegradable and biocompatible, and cotton linter is an inexpensive biodegradable filler regionally available. Thus, PCL/cotton linter compounds may be of interests as an environmentally-friendly substitute of material currently used in many applications.

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In this work PCL/cotton linter compounds were melt extruded and test samples injected with filling content ranging from 1% to 5% of the weight.

The main objective of producing PCL/cotton linter compounds was to make a material 100% biodegradable using as filling a regional byproduct, costing less than neat PCL matrix, with similar processing conditions and the same machinery.

Properties and morphology of neat PCL and its compounds were investigated by means of torque rheometry, heat deflection temperature (HDT), thermogravimetry (TG), differential scanning calorimetry (DSC), X ray diffraction (XRD), scanning electron microscopy (SEM), mechanical tests in tension, flexion and impact.

This paper presents as novelty the use of cotton linter and nanolinter, which are byproducts of the cotton culture, as filling for PCL compounds. According to the results forward presented these compounds have improved thermal stability and mechanical properties, costing less than neat PCL. It is also worth mentioning that the use of cotton linter is an income source for the poor population in the northeast region of Brazil.

2. Experimental

2.1. Materials

Poly (ϵ -caprolactone) (PCL) trade name CAPA 6500, with molar mass (M) 47500 g/mol and viscosity (η) 2890 Pa.s (70°C, 10 l.s⁻¹) was purchased from Perstork.

Raw cotton linter was kindly supplied by Embrapa Cotton, Campina Grande/Paraíba/Brazil. It was obtained from cotton Delta Opal, harvested in State of Bahia, Brazil, 2010, under environmental conditions of the *cerrado* (Brazilian savannah).

Cotton nanolinter was produced by acid hydrolysis of raw cotton linter. The acid hydrolysis procedure used to make the nanolinter is described in Moraes et al (2013)¹⁴. It was kindly supplied by Embrapa Tropical Agroindustry, Fortaleza/Ceará/Brazil. It is expected that the use of nanoparticulate filler will improve the performance of the compound compare with the conventional micro compound, i.e. untreated cotton linter.

Figure 1 shows cotton linter and cotton nanolinter samples used to prepare PCL compounds.

2.2. Methods

2.2.1. Improvement of raw cotton linter

As received raw cotton linter was washed several times in a decantation apparatus connected to a compressor (at 3 Bar) to take off the impurities, and then it was brushed and used to make the PCL compounds, processing occurred at room temperature.

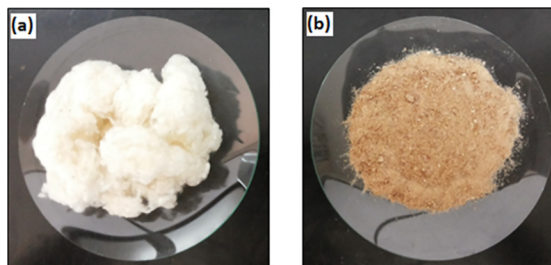


Figure 1: Cotton linter (a) and nanolinter (b) as used to make PCL compounds.

2.2.2. Processing

Concentrates of 95/5 PCL/cotton linter and 95/5 PCL/cotton nanolinter were made by melt mixing in a thermokinetic mixer model MH-50H; and ground in a knife mill. The concentrates were diluted to final cotton linter and cotton nanolinter concentrations of 1%, 3% and 5% w/w with neat PCL in a corotating twin screw extruder Coperion-Werner&Pfleiderer ZSK 18 operating at 80-90°C and 180 rpm, followed by grinding in a knife mill. Same procedure was applied to neat PCL.

Specimens of PCL/cotton linter and PCL/cotton nanolinter at 99/1, 97/3 and 95/5 w/w for tensile, impact, flexion, and heat deflection temperature testing according to ASTM D638, ASTM D256, ASTM D790 and ASTM D648 standards were injection molded in a Fluidmec H 30/40 at 60-70°C. Neat PCL specimens were injected using the same procedure for means of comparison¹⁵.

Compounds studied in this work were named as PCL/Cotton linter (1%), PCL/Cotton linter (3%), PCL/Cotton linter (5%), PCL/Cotton nanolinter (1%), PCL/Cotton nanolinter (3%), PCL/Cotton nanolinter (5%), in parenthesis is cotton linter and cotton nanolinter content by weight.

2.2.3. Characterization

2.2.3.1. Lignocellulosic analysis

The content of moisture, ash, extractives, lignin, hemicellulose, and alpha-cellulose was measured in the raw cotton linter samples applying the procedure reported elsewhere¹⁴.

2.2.3.2. Particle size and zeta potential measurements

Particle size carried out by dynamic light scattering and potential zeta measurements were done using a Zetasizer Nano ZS (Malvern).

2.2.3.3. X-ray diffraction (XRD)

X-ray diffraction (XRD) experiments were executed in a Shimadzu XRD-6000 instrument in the region of 2-30° (2 θ), with K _{α} Cu radiation, tension 40 kV, current 30 mA and scan rate 2°/min.

2.2.3.4. Torque rheometry

Neat PLC, PLC/Cotton linter and PLC/Cotton nanolinter compounds with 1%, 3%, and 5% of cotton linter content, were processed in a HaakeRheomix 600 laboratory internal mixer at 60 rpm for 20 minutes, with the chamber wall kept at 80°C. Torque and temperature as functions of time were plotted for PCL and its compounds.

2.2.3.5. Thermogravimetry (TG)

Thermogravimetry analyses were performed in a TA Instruments SDT-Q600, samples with 5 mg were heated at 10°C/min from ambient temperature (23°C) to 1000°C under nitrogen flow of 50 mL/min.

2.2.3.6. Differential Scanning Calorimetry (DSC)

DSC analyses carried out in a Shimadzu DSC-50, samples with approximately 5 mg were heated from 23°C to 80°C, followed by an isothermal stage of 3 minutes and then cooled to 10°C, with a heating/cooling rate 10°C/min, under nitrogen flow of 50 mL/min.

2.2.3.7. Heat deflection temperature (HDT)

Heat deflection temperature tests carried out in a HDT 6 VICAT P/N 6921.000 instrument according to ASTM D648. Experiments were conducted at load 455 kPa, heating rate 120°C/h (method A), specimens were immersed into silicone bath oil and HDT was determined at 0.25mm of specimen deflection. Presented results are the average of five tests.

2.2.3.8. Mechanical tests

Mechanical properties in tension were measured according to ASTM D638; tests were conducted in an EMIC DL 10000 testing machine operating at 50 mm/min elongation rate and 200 kgf load. Presented results are an average of ten tests.

Mechanical properties in flexion were measured according to ASTM D790, tests were executed in a universal machine Shimadzu AG-X 50KN with cell charge 20 kN, operating at 5 mm/min and initial force 29N. Presented results are an average of five tests.

Mechanical properties in impact were measured according to ASTM D256, tests were performed in a CEAST Resil-5.5 impact machine operating with a 2.75J pendulum on notched specimens in Izod configuration. Presented results are an average of ten tests.

All mechanical tests were executed in ambient temperature (23°C)

2.2.3.9. Scanning electron microscopy (SEM)

Scanning electron microscopy images were acquired in a SSX 550 Superscan-Shimadzu. Fractured surface from impact test was covered with gold to avoid accumulation of charges.

3. Results and Discussion

3.1. Lignocellulosic analysis

Table 1 shows cotton linter components determined by lignocellulosic analysis. Cotton linter presented low levels of humidity, ash and lignin, whereas a high content of cellulose was reached. Based on these data and according to literature cotton linter can be assumed as a promising material to make the PCL compounds¹⁶⁻¹⁹.

Table 1: Lignocellulosic composition of cotton linter.

Components	Percentage (%)
Humidity	5,3 ± 0,1
Ash	1,5 ± 0,0
Lignin	5,9 ± 0,0
Holocellulose*	87,5 ± 1,2
Alpha-cellulose	83,9 ± 0,6
Hemicellulose	3,6 ± 0,6

3.2. Particle size and zeta potential measurements

Potential zeta measurement was done to verify if cotton nanolinter trends to flocculate, results of potential zeta and particle size are shown in Table 2. Negative value (-50 mV) obtained probably is due to hydroxyl esterification of carbohydrates with sulfate groups, which are anionic; with this value in modulus higher than 25 mV, the nanocellulose solution can be assumed as stable, meaning it doesn't have a tendency to flocculate^{14, 20}.

Table 2: Zeta potential, particle size and yielding of nanocrystals of cotton linter.

Zeta Potential (mV)	-50,0
Percentage of particles, < 100 nm (%)	7,2
Average particle size, < 100 nm (nm)	89,7
Percentage of particles, 100-1000 nm (%)	92,2
Average particle size, 100-1000 nm (nm)	319,5
Yielding (%)	29,4

Regarding particle size evaluation, 92.2% of it is between 100-1000 nm and these were cotton nanolinter particles used in this work. According to yielding results for each kilo of cotton linter subjected to acid hydrolysis, 294 grams of cotton nanolinter are produced.

3.3. X ray diffraction (XRD) measurements

Figure 2 shows X ray diffratograms of PCL, cotton linter, cotton nanolinter, and PCL/cotton linter and PCL/cotton nanolinter compounds.

PCL presented peaks around 21.1° and 23.5° corresponding to basal distance of 0.42 nm and 0.38 nm for the 110 and 200 planes²¹⁻²⁴.

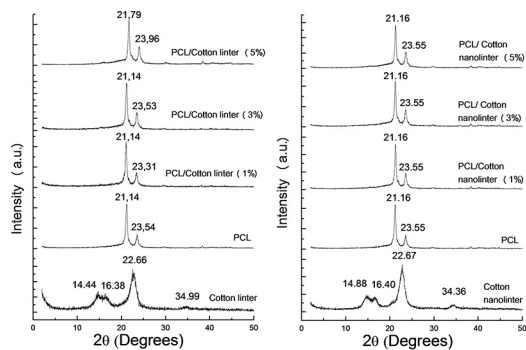


Figure 2: X ray diffratograms cotton linter, cotton nanolinter, PCL, PCL/cotton linter and PCL/cotton nanolinter compounds. Cotton linter and its compounds (a), Cotton nanolinter and its compounds (b) (Compositions indicated).

Cotton linter and cotton nanolinter presented peaks around 14.44° , 16.38° , 22.66° e 34.99° , corresponding to basal distance of 0.31 nm, 0.27 nm, 0.20 nm and 0.13 nm. According to literature they are evidences of cellulose type I and may be attributed to (101), (10 $\bar{1}$), (002) and (004) planes. These results indicated that acid hydrolysis did not change the crystalline character of cotton linter. Moreover, the crystalline character of PCL didn't change upon addition of cotton linter or cotton nanolinter²⁵⁻²⁶.

3.4. Torque rheometry measurements

Torque rheometry was used to investigate the thermal stability of PCL and its compounds with cotton linter and cotton nanolinter during processing. Torque value is directly proportional to the polymer viscosity, at constant processing conditions, namely temperature and rotor speed, results of torque may be understood as an indirect measure of molecular weight. Falling down of torque at constant temperature means decreasing in molecular weight, suggesting that polymer degradation took place during processing. A constant torque plateau indicates the absence of degradation²⁷⁻²⁸.

Figure 3 shows temperature and torque versus time plots for PCL/cotton linter and PCL/cotton nanolinter compounds. PCL and its compounds showed constant temperature and torque plateaus for 20 minutes processing time, with no evidence of degradation.

3.5. Thermogravimetry (TG) Measurements

Thermal stability and degradation mechanisms of cotton linter, cotton nanolinter, PCL and its compounds were investigated by thermogravimetry (TG). Figure 4 presents TG and differential thermogravimetry (DTG) plots for the compositions tested in this work.

Cotton linter and cotton nanolinter presented similar behaviour in TG plots, around 100°C is observed the first event due to water release corresponding to 8% of weight loss. A second event is verified around 300°C , it is observed

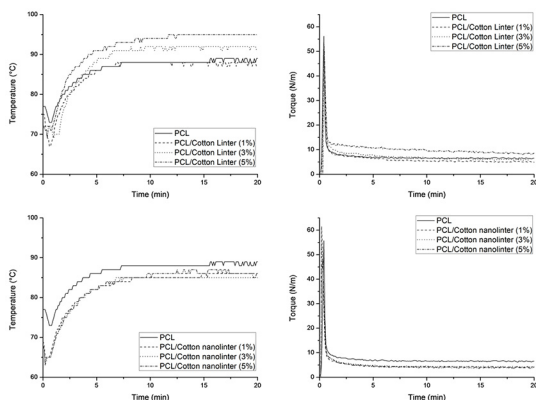


Figure 3: Temperature (left: a and c) and torque (right: b and d) versus time for PCL/cotton linter and PCL/cotton nanolinter compounds. Compositions indicated.

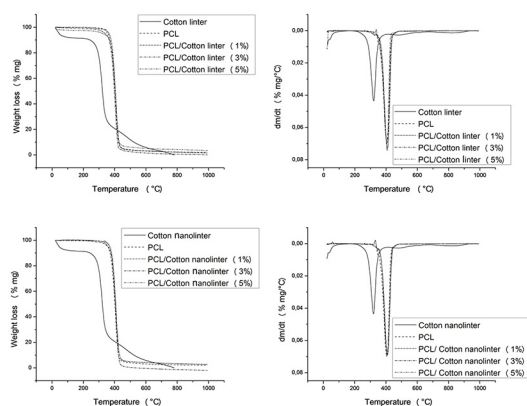


Figure 4: TG and DTG plots for cotton linter, cotton nanolinter, PCL, PCL/cotton linter and PCL/cotton nanolinter compounds. (Compositions indicated).

as a peak between 200°C and 400°C in DTG plots and it is associated with pyrolysis of cellulose, lignin and hemicellulose and corresponds to 90% of weight loss. The third event is due to degradation of residual lignin taking place around 700°C . From TG and DTG plots is verified that the acid hydrolysis did not change the thermal stability of cotton linter²⁹⁻³³.

TG plots of PCL presented decomposition in one stage starting around 260°C , this decomposition is visualized in DTG plots as a peak with maximum height at 405°C . The residual content at the end of thermal analysis was 2%.

PCL/cotton linter and PCL/cotton nanolinter compounds presented TG and DTG plots very similar to that of neat PCL, with plots showing decomposition in one event, the weight loss started around 260°C and the maximum degradation rate was observed around 400°C in DTG plots. These results mean that the thermal stability of PCL wasn't changed upon addition of cotton linter, although cotton linter has a lower thermal stability compared with PCL.

3.6. Differential scanning calorimetry (DSC) measurements

Figure 5 shows endotherms of fusion and exotherms of melt crystallization for PCL and PCL/cotton linter and PCL/cotton nanolinter compounds, and Table 3 presents thermal parameters acquired from DSC scans. Apparently, adding cotton linter / cotton nanolinter had mild effect on PCL fusion, all endotherms presented simple peaks indicating that fusion takes place in a single event. Usually, biodegradable polymer as example PHB present complex peaks during fusion due to different morphologies, crystallite sizes and stabilities; however in the present work neither cotton linter nor cotton nanolinter changed the thermal character of PCL. Although the acid hydrolysis to which cotton linter was subjected with the intention of generating new reactive groups and chemical links between PCL and cotton nanolinter, seemingly it was not strong enough to create new populations of crystals³⁴⁻³⁶.

Concerning the crystallization peak, it became narrower and sharper upon filling addition; this result suggests an increase in polymer homogeneity. Higher degree of crystallinity was observed for the compounds with 1% and 3% nanolinter. The maximum crystallization peak took place earlier for compounds with nanolinter, an increase around 30% was observed for this parameter, suggesting the melt crystallization occurred earlier in cotton nanolinter compounds, possible due a nucleant effect. It is known from literature that addition of filling to polymer may result in nucleant effect. It is possible that cotton linter and cotton nanolinter are behaving as nucleant during PCL crystallization. In general, the observed enthalpy of crystallization and the crystallinity results suggest that these parameters were not significantly affected by the presence and concentration of the fillers^{35,37}.

3.7. Mechanical properties evaluation

Mechanical properties in tension for PCL and its compounds with cotton linter and cotton nanolinter are showed in Figure 6. PCL is a ductile polymer as its elongation

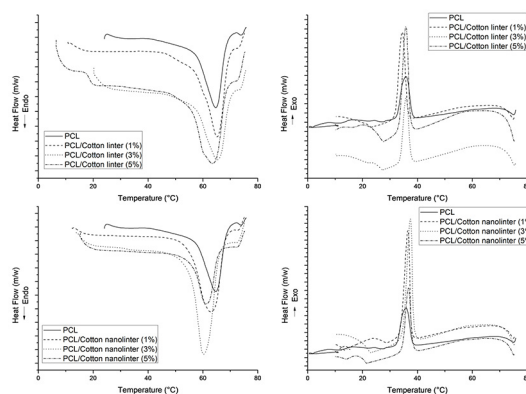


Figure 5: Melt endotherms and Crystallization exotherms for PCL/ cotton linter and PCL/cotton nanolinter compounds. Compositions indicated.

at break was 418.6 %, upon addition of cotton linter this property increased to values higher than 430%, and for the compositions with 1% and 3% the experiment reached the machine limit without rupture taking place.

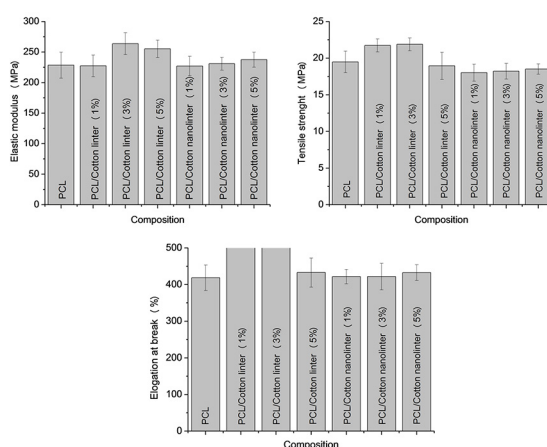


Figure 6: Mechanical properties in tension: Elastic modulus, Tensile strength and Elongation at break of PCL, and PCL/Cotton linter and PCL/Cotton nanolinter compounds. Compositions indicated.

Table 3: Characteristic temperatures, enthalpies of fusion and crystallization, and degree of crystallinity for PCL/cotton linter and PCL/cotton nanolinter compounds.

Compositions	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	X_c (%)
PCL	65.0	- 56.8	30.0	39.6	40.7
PCL/cotton linter (1%)	65.5	- 67.2	29.9	48.3	47.7
PCL/cotton linter (3%)	65.5	- 55.8	29.9	40.1	38.8
PCL/cotton linter (5%)	63.9	- 67.9	32.9	47.7	46.2
PCL/cotton nanolinter (1%)	63.2	- 69.9	36.6	50.8	49.6
PCL/cotton nanolinter (3%)	60.3	- 78.2	38.9	59.5	54.3
PCL/cotton nanolinter (5%)	61.3	- 53.2	38.6	39.9	36.2

T_m = Temperature of melting peak; ΔH_m = Melting enthalpy; T_c = Temperature of crystallization peak; ΔH_c = Enthalpy of crystallization; X_c = Degree of crystallinity, ($X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100$); ΔH_m^0 = Equilibrium melting enthalpy; $\Delta H_m^0 = 139.5 \text{ J/g}$ ³⁸.

Regarding elastic modulus results, an increase of 12% and 16% was observed for the PCL compounds with 3% and 5% of cotton linter, compounds with cotton linter 1% and 3% presented strength stress increased by 12%. None reasonable effect in tensile properties of adding cotton nanolinter to PCL was verified as presented in Figure 6.

In principle, these results are encouraging, once lower cost filling was added to PCL, promoting an increasing in its thermal stability (HDT, Figure 9), tensile strength and elongation at break (Figure 6). Probably these properties are linked to a well dispersed cotton linter (fibrils) and cotton nanolinter (particles) within the PCL matrix (see SEM images in Figures 13 and 14). That was obtained due to appropriated processing conditions^{16,39-40}.

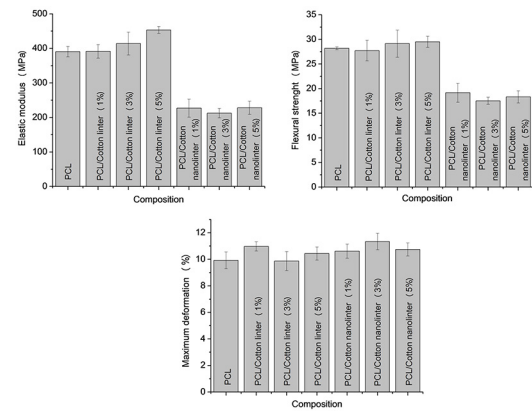


Figure 7: Mechanical properties in flexion: Elastic modulus, Tensile strength and Elongation at break of PCL, and PCL/cotton linter and PCL/cotton nanolinter compounds. Compositions indicated.

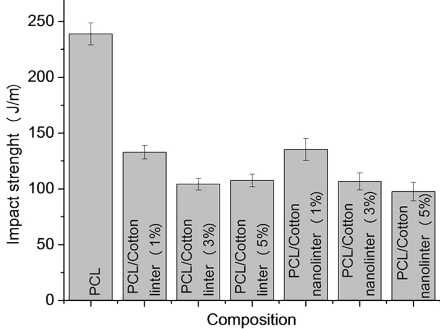


Figure 8: Impact strength of PCL, and PCL/cotton linter and PCL/cotton nanolinter compounds. Compositions indicated.

Mechanical properties in flexion for PCL and its compounds with cotton linter and cotton nanolinter are showed in Figure 7. Adding nanolinter to PCL decreased its elastic modulus and flexural strength with slight effect on maximum deformation. For three cotton nanolinter contents investigated in this work similar results for flexion experiments

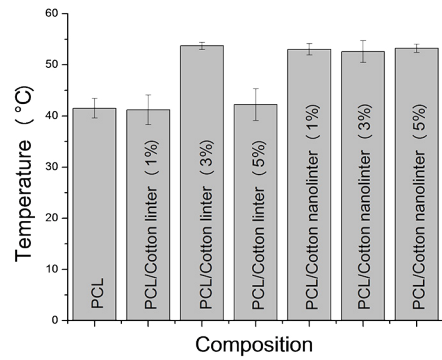


Figure 9: HDT measurements of PCL, PCL/cotton linter and PCL/cotton nanolinter compounds.

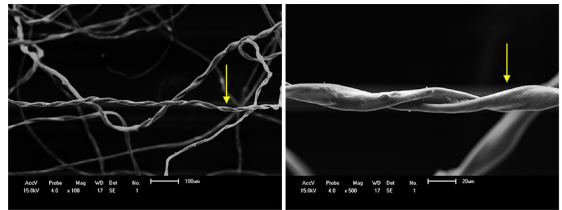


Figure 10: SEM images of Cotton linter fibrils. (Scale bar: 100 μm and 20 μm).

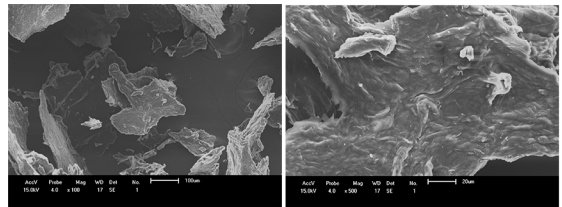


Figure 11: SEM images of Cotton nanolinter particles. (Scale bar: 100 μm and 20 μm).

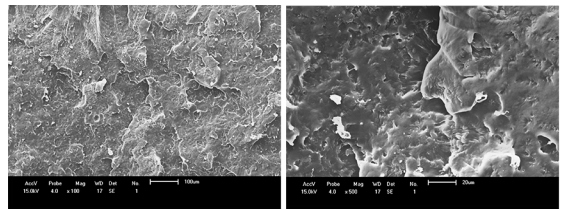


Figure 12: SEM image of fractured surface of PCL. (Scale bar: 100 μm and 20 μm).

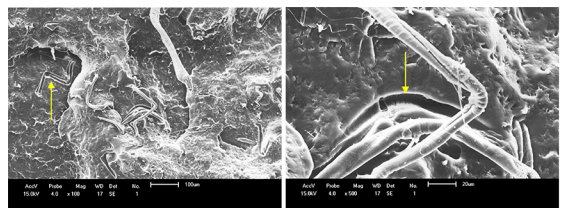


Figure 13: SEM image of fractured surface of PCL/cotton linter (1%). (Scale bar: 100 μm and 20 μm).

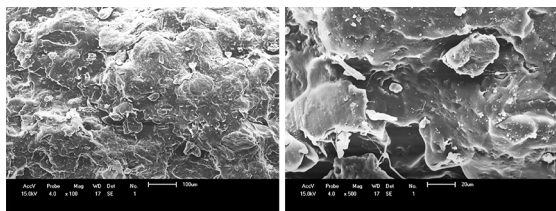


Figure 14: SEM image of fractured surface of PCL/cotton nanolinter (5%). (Scale bar: 100 μm and 20 μm).

were obtained. Nevertheless, increases of 6% and 16% were observed in elastic modulus of PCL/cotton linter (3%) and PCL/cotton linter (5%) compounds, respectively, whereas no change was verified in flexural strength and maximum deformation for PCL compounds with cotton linter. The reduction in the Elastic Modulus, Flexural Strength and Impact Strength (see Figure 8) of nanolinter compounds compared with conventional cotton linter compounds may be explained in part by possible increase of tension concentration regions originated the nanoparticles as well as by aggregation mechanisms. Flexion experiments may be used to define bending tolerance of polymer products; for this specific use compounds with cotton linter should be chosen instead of cotton nanolinter compounds.

Mechanical properties in impact for PCL and its compounds with cotton linter and cotton nanolinter are showed in Figure 8. All compounds processed in this work presented lower impact strength than neat PCL, decreases of 59%, 55% and 43% were acquired for compositions with 1%, 3% and 5% of cotton nanolinter; and decreases of 55%, 56% and 44% were acquired for compositions with 1%, 3% and 5% cotton linter. PCL as showed above is a ductile polymer with higher impact strength.

Impact strength is a measurement of energy dissipation during short term deformation in polymeric solids. It is believed that in PCL compounds the added fibrils and particles may be acted as stress concentrators hindering the energy dissipation mechanisms to work properly thus lowering the impact strength.

3.8. Heat deflection temperature (HDT) measurements

Figure 9 presents HDT results for PCL and its compounds with cotton linter and cotton nanolinter. Compounds upon addition of cotton nanolinter presented temperatures approximately 20% higher than neat PCL and PCL/cotton linter compounds. In general, adding natural fibers to polymers increases its brittle character, normally changing its strain behavior; an interesting result obtained in this work was the increase in HDT values of cotton nanolinter compounds with no change in strain at break values (see Figure 6). This increase in HDT values indicates that the acid hydrolysis was successful, and may result in an increase in the use temperature of PCL products^{39,41-42}.

It was not observed significant difference in mechanical and thermal properties between nanolinter and conventional linter compounds. Consequently, the use of the more expensive, chemically modified filler is not justified.

3.9. Scanning Electron Microscopy (SEM) Images

SEM images of cotton linter used in this work to make PCL compounds are shown in Figure 10. It presented an interlacing fibril structure with high L/D (length/diameter) ratio. In Figure 11 is showed images of cotton nanolinter, a drastic structural change is verified, provoked by acid hydrolysis; cotton nanolinter show a particulate structure with some aggregates; although the acid hydrolysis didn't change the crystalline and thermal character of cotton linter (see Figures 2, 4 and 5) it modified its morphological structure.

Figure 12 shows SEM images of PCL that presents a ductile fracture with several zones of plastic deformation, which agrees with strain results shown in Figure 6.

Figure 13 presents SEM images of PCL/cotton linter (1%). Clearly, a matrix/fibrils morphology could be seen; upon fracture some fibrils remained attached to PCL matrix while others were detached from it. In general cotton linters fibrils were well dispersed in PCL matrix promoting the good properties of PCL compounds as mentioned above.

SEM images of PCL/cotton nanolinter (5%) are showed in Figure 14. A particulate structure embedded within PCL matrix is verified, the acid hydrolysis to which raw cotton linter was subjected changed it shape from fibrils to particle as earlier described. This structure is easily observed in Figure 14. Particle aggregates were obtained probably due to the lower miscibility between PCL and cotton nanolinter; however, they weren't strong enough to compromise the mechanical performance and thermal stability of PCL, as mechanical (Figure 6) and HDT (Figure 9) results showed.

4. Conclusions

PCL/cotton linter and nanolinter compounds studied in this work showed properties similar to neat PCL. Higher ductility was reached in compounds with cotton linter whereas higher HDT was got in nanolinter systems, suggesting the possibility of higher use temperature. The increase in the crystallization temperature suggests shorter processing time. Fillers are less expensive than the matrix thus the researched compounds present attractive alternative to neat PCL.

5. Acknowledgments

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for supplying the cotton nanolinter, and to Federal University of São Carlos Polymer Laboratory for HDT experiments.

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