

## Effect of organoclay and corn straw on the properties of polycaprolactone composite films

Efeito de argila organofílica e palha de milho nas propriedades de filmes compósitos de policaprolactona

Efecto de la organoarcilla y la paja de maíz en las propiedades de películas compuestas de policaprolactona

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### **Abstract**

The packaging industry requires materials capable of offering barriers to the entry of microorganisms, with the ability to protect and maintain the characteristics of the packaging content. The use of fillers can enhance these barrier properties to the polymeric material. This work investigates the effect of incorporating different fillers (organophilic clay and corn straw) on the rheological, thermal, mechanical and permeability characteristics of polycaprolactone (PCL) processed in an internal laboratory mixer. The results of torque rheometry suggest polymer matrix degradation during processing did not increase, nor the thermal stability of the matrix. Composite films showed higher tensile strength, higher stiffness and lower elongation. Incorporation of the fillers in the PCL matrix reduced the permeability to oxygen and carbon dioxide gases of the produced films. Adding up to 1% of organoclay C20A or corn straw to PCL leads to a material that combines maintenance or improvement of properties combined with lower permeability to oxygen and carbon dioxide, which confirms the potential use of these systems in packaging industry.

**Keywords:** PCL; Organophilic clay; Corn straw; Composites; Permeability.

### **Resumo**

A indústria de embalagens necessita de materiais capazes de oferecer barreiras à entrada de microrganismos, com capacidade de proteger e manter as características do conteúdo. O uso de cargas pode melhorar essas propriedades de barreira ao material polimérico. Este trabalho investiga o efeito da incorporação de diferentes cargas (argila organofílica e palha de milho) nas características reológicas, térmicas, mecânicas e de permeabilidade da policaprolactona (PCL) processada em misturador interno de laboratório. Os resultados da reometria de torque sugerem que a degradação da matriz polimérica durante o processamento não aumentou, nem a estabilidade térmica

da matriz. Os filmes compósitos apresentaram maior resistência à tração, maior rigidez e menor alongamento. A incorporação das cargas na matriz PCL reduziu a permeabilidade aos gases oxigênio e dióxido de carbono dos filmes produzidos. A adição de até 1% de argila organofílica C20A ou palha de milho ao PCL resulta em um material que combina a manutenção ou melhoria das propriedades aliada à menor permeabilidade ao oxigênio e ao dióxido de carbono, o que confirma o potencial de uso desses sistemas na indústria de embalagens.

**Palavras-chave:** PCL; Argila organofílica; Palha de milho; Compósitos; Permeabilidade.

### Resumen

La industria del packaging necesita materiales capaces de ofrecer barreras a la entrada de microorganismos, con capacidad de proteger y mantener las características del contenido. El uso de cargas puede mejorar estas propiedades de barrera del material polimérico. Este trabajo investiga el efecto de la incorporación de diferentes rellenos (arcilla organofílica y cascarilla de maíz) sobre las características reológicas, térmicas, mecánicas y de permeabilidad del policaprolactona (PCL) procesado en un mezclador interno de laboratorio. Los resultados de la reometría de par sugieren que la degradación de la matriz polimérica durante el procesamiento no aumentó, ni tampoco la estabilidad térmica de la matriz. Las películas compuestas mostraron mayor resistencia a la tracción, mayor rigidez y menor elongación. La incorporación de los rellenos en la matriz de PCL redujo la permeabilidad a los gases de oxígeno y dióxido de carbono de las películas producidas. La adición de hasta un 1% de arcilla organofílica C20A o paja de maíz al PCL da como resultado un material que combina el mantenimiento o mejora de propiedades aliadas a una menor permeabilidad al oxígeno y al dióxido de carbono, lo que confirma el potencial del uso de estos sistemas en el envasado. industria.

**Palabras clave:** PCL; Arcilla organofílica; Cascarilla de maíz; Compuestos; Permeabilidad.

## 1. Introduction

Producing biodegradable films to be used as packaging, becomes a current way to reduce the problem of accumulation of plastic materials in the environment, since biodegradables are able to degrade in relatively short times compared to conventional polymers generally used in packaging. One of these polymers is polycaprolactone (PCL), which despite being derived from petroleum, is a highly biodegradable, biocompatible and hydrophobic polymer (Fakhouri et al., 2009; Nicácio et al. 2022).

The formation of composites using montmorillonite clays as reinforcing material for polymers, due, among other factors, to the possibility of intercalation/exfoliation of the silicate layers in the polymer matrix, as well as the natural fiber, has promoted improvements in the properties of the final material, including with the improvement in the barrier properties of polymeric films (Bettio & Pessan, 2012; Luna et al., 2022).

PCL is a biodegradable aliphatic polyester with low melting point and high elasticity (Matta et al., 2014) often used as an additive in order to accelerate degradation of polymer composites and blends. Due to its slow degradation in vivo, it is quite suitable for controlled release devices and can be applied in films for food packaging, thermoformed, injected, blown and extruded artifacts (Averous & Pollet, 2012; Luna et al., 2021).

Corn straw is a plant fiber composed mainly of cellulose, lignin and hemicellulose, which has relatively high modulus and tensile strength, having the potential to be used as reinforcement in composites and demonstrating its potential for industrial use (Guimarães et al., 2010). Brazil is a country with high agricultural production and, therefore, assiduous waste production. Corn is one of the main existing agricultural products, being the most produced cereal in the world. With regard to corn production, according to a survey by the National Supply Company (Conab), Brazil is the third largest producer in the world, with production estimated at 99.984 million tons between 2018 and 2019. This number represents growth of 23.9% over last season, when the country harvested 80.709 million tons.

The properties of composite materials, in general, are superior to the properties of the neat polymer. The use of corn straw and organophilic clay, forming PCL composites, allows a significant increase in mechanical properties, maintaining some characteristics and advantages of the two different types of fillers. Researching the possibilities of combinations of these

loads is important in order to optimize the performance of composites, extracting their potential to the maximum, which makes it important to research this type of material, exploring its real potential and possible industrial application.

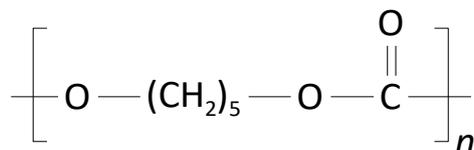
The research of materials for the development of packaging must observe the ability to protect and maintain the characteristics of the products contained therein. Thus, studying the permeability to different gases of these films produced is an indication of the protection capacity that the film can offer to the contents of the packages (Bardi et al., 2014).

Therefore, the purpose of this work is to innovate in the development of biodegradable PCL composite films using organophilic clay and corn husk vegetable fiber as fillers and, in this way, to evaluate the effect of different types and contents of fillers on the structure, properties barrier, thermal, rheological, mechanical properties of these composites, and thus collaborate with the development of new materials from PCL, expanding and innovating the alternatives for its application in the plastic film sector.

## 2. Methodology

The polymeric matrix employed was polycaprolactone (PCL), trade name Capa™ 6500 supplied by Perstorp (Sweden) purchased from MCassab, density of 1.145 g/cm<sup>3</sup> at room temperature, with a melt flow rate of 1.6–2.2 dg/min (ISO 1133, 190 °C/2.16 kg), melting point between 58 and 60°C and crystallinity of 35-40%, according to the manufacturer (Mohanty et al., 2005; Perez et al., 2008). The chemical structure of PCL is shown below in Figure 1.

**Figure 1** – Chemical structure of PCL.



Source: Authors.

The organoclay used was Cloisite®20A (C20A) purchased from Southern Clay Products (USA). It is a natural layered silicate (montmorillonite) with cation exchange capacity 0.95 meq/g, modified with quaternary ammonium salt with two long-chain (C<sub>16</sub> to C<sub>18</sub>) aliphatic residues. It has a basal interplanar distance of 2.42 nm and a density of 1.72 g/cm<sup>3</sup>, average particle diameter of 8.2 μm, with 80% of the particles ranging in size from 1.7 to 15.7 μm (Falcão et al., 2017).

Corn straw (CS) collected from Campina Grande/PB (Brazil) was used as lignocellulosic vegetable filler, without pre-processing. The true density of the filler is 1.157 ± 0.06, measured with hexane in a pycnometer at ambient temperature (Reul et al., 2018).

Samples with 1, 3 and 5% organoclay and corn straw content (by weight) were prepared in a Haake Rheomix 3000 laboratory internal mixer, fitted with high-intensity (roller type) rotors. The processing chamber wall was kept at a constant temperature of 150°C and the fill factor was estimated at 75%. The mixer was operated at 60 rpm for 12 min. Samples of the neat PCL matrix were also processed to provide a baseline for comparison. The compounds were ground and fed to a 16 mm bench scale single screw extruder Lab-16 Chill-Roll from AX Plásticos (Brazil) with a flat die, operating at 150°C and 45 rpm, to prepare films for further characterization. Film thickness between 95 and 138 μm was measured for the different compounds.

Differential scanning calorimetry (DSC) tests were led in Mettler Toledo, with film samples of approximately 5 mg in an inert atmosphere, following a thermal program in three stages: heating from 25°C to 100°C, cooling to 0°C and reheating to 100°C, at a heating/cooling rate of 10°C/min. The raw time-temperature-heat flow data were integrated using custom software

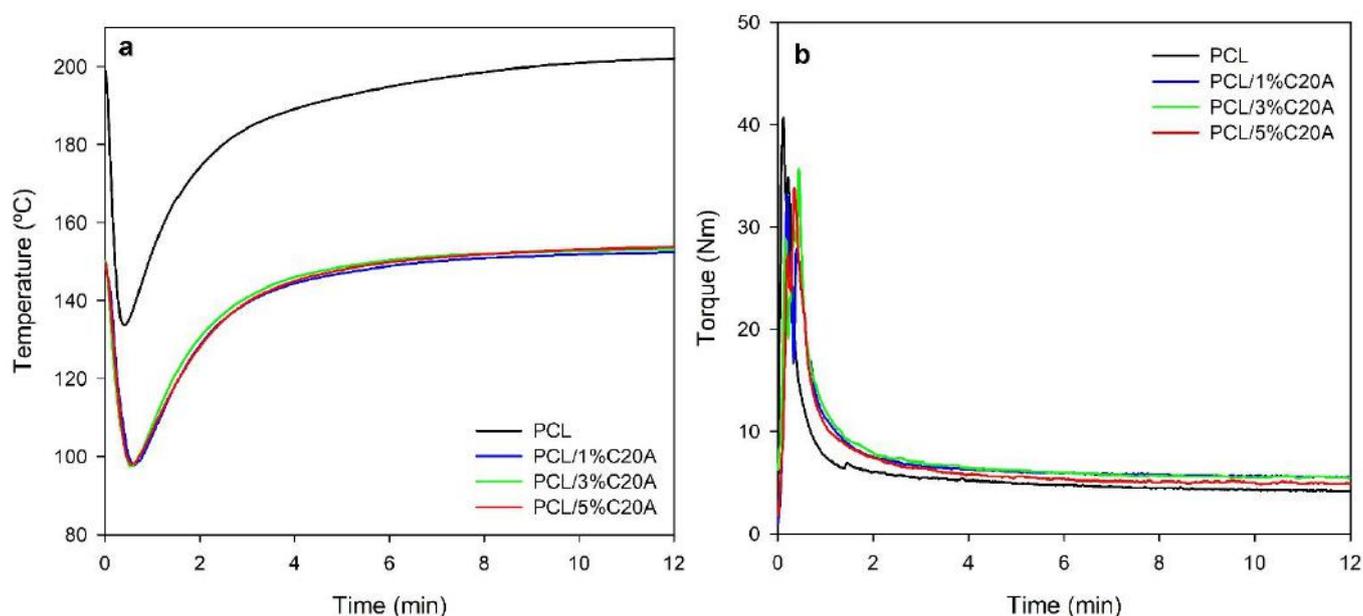
and thermal parameters (temperatures and rates, crystallinity, etc) computed for all phase-transition events detected. Permeability to oxygen and carbon dioxide gases were measured at 25°C in a GPD-C Brugger instrument according to ASTM D1434 e ISO 15105/1 standards. Tensile tests were done according to ASTM D882-02, using an Instron 5982 machine with a 5 kN load cell operating at 25 mm/min constant rate of extension at ambient temperature.

### 3. Results and Discussion

#### 3.1 Torque Rheometry

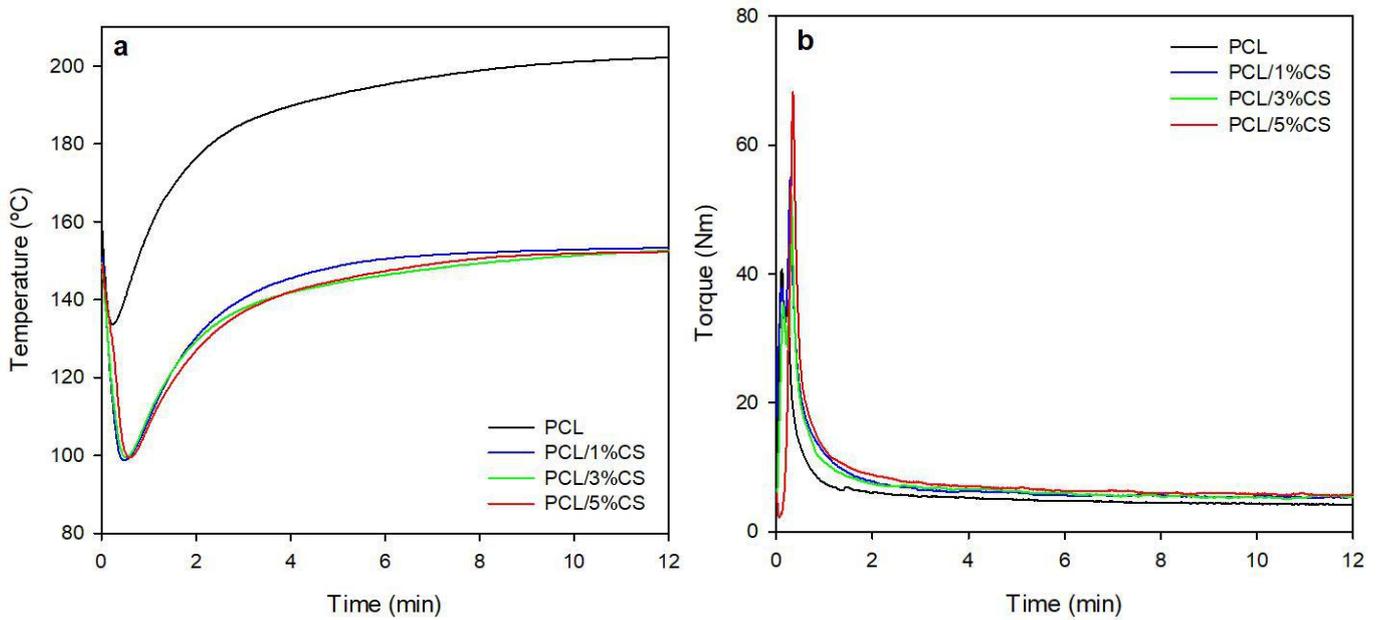
Temperature inside the processing chamber (T) and total torque (Z) were measured as a function of time (t) during compounding in the internal mixer. Results are presented in Figures 2 and 3.

**Figure 2** – Temperature (a) and torque (b) as function of time in the internal mixer chamber to PCL/C20A composites.



Source: Authors.

**Figure 3** – Temperature (a) and torque (b) as function of time in the internal mixer chamber to PCL/CS composites.



Source: Authors.

A drop in the temperature is observed up to 4 min of processing, associated with the introduction of inputs into the processing chamber. The plots suggest that after 4 min the matrix is substantially molten. Torque changes due to increasing degree of dispersion (if any) are negligible during the final stage of melt processing, identified here as the last four minutes inside chamber (8 to 12 min processing time). Since at constant rotor speed torque is directly proportional melt viscosity at this stage, decrease of torque with time may be attributed to increases in melt temperature and decreases in molar mass of the polymer due to degradation during processing (Canedo, 2017).

According to Canedo (2017), the relative rate of change of the adjusted torque is considered as a measure of the degradation rate. Temperature effects on the viscosity (that is, on torque) may be eliminated by adjusting the torque to a constant reference temperature ( $T^*$ ):

$$Z^* = Z \exp\{\beta(T - T^*)\} \quad (1)$$

where  $Z^*$  is the adjusted torque and  $\beta$  is the exponential temperature coefficient of the viscosity, taken here as  $0.012^\circ\text{C}^{-1}$  (Reul et al., 2018). Table 1 presents the calculated parameters in the final interval of processing (8-12 min) at  $150^\circ\text{C}$ . These include, respectively, the average temperature and adjusted torque in that range ( $\bar{T}$  and  $\bar{Z}^*$ ) and two versions of the degradation rate: the relative rate of reduction of the adjusted torque ( $R_z$ ) and the relative rate of reduction of weight average molar mass ( $R_M$ ), evaluated according to the procedure described to Canedo (2017).

**Table 1** – Torque rheometry parameters during the final stage (8-12 min).

Sample	$\bar{T}$ (°C)	$\bar{Z}^*$ (Nm)	$R_z$ (min <sup>-1</sup> )	$R_M$ (min <sup>-1</sup> )
PCL	201.6 ± 0.4	5.5 ± 0.5	0.006	0.002
PCL/1% C20A	152.2 ± 0.2	10.8 ± 0.0	0.231	0.013
PCL/3% C20A	153.0 ± 0.1	10.8 ± 0.1	0.046	0.036
PCL/5% C20A	153.5 ± 0.2	10.3 ± 0.1	0.126	0.067
PCL/1% CS	154.2 ± 0.1	10.9 ± 0.1	0.548	0.159
PCL/3% CS	153.0 ± 0.0	10.3 ± 0.1	1.228	0.356
PCL/5% CS	154.0 ± 0.0	10.4 ± 0.1	1.270	0.368

Source: Authors.

The results in Table 1 show that PCL and composites are quite stable and degrade minimally during processing. The torque adjusted in the neat polymer, when compared to all composites, increases up to 50%, being 5.5 Nm for the neat PCL and reaches to 10.9 Nm for the PCL/1% CS composite. Analyzing the adjusted torque, as different loads were inserted into the matrix, an increase in the adjusted torque was obtained and, consequently, an increase in viscosity. In general, the viscosity of solid particle dispersions in stable molten matrices is greater than the viscosity of the neat matrix and increases with filler content. It is observed that the viscosity of neat PCL is lower than all the viscosities of the composites and that the viscosity of the composites did not vary significantly with the filler content.

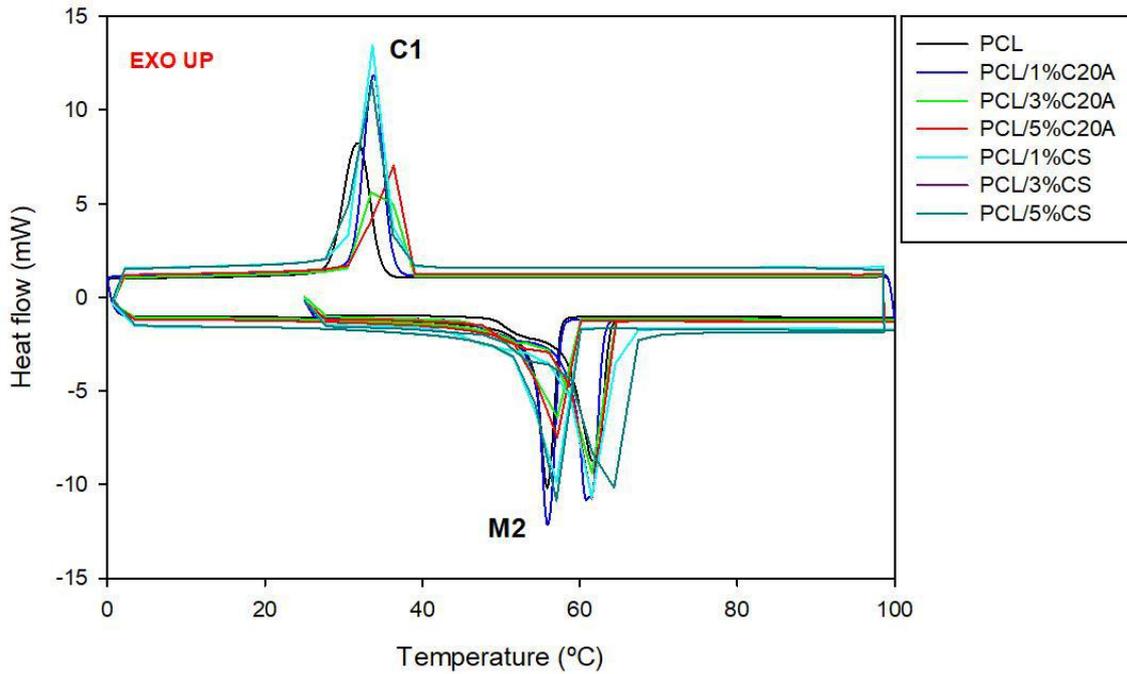
The incorporation of both clay and vegetal fiber slightly increased the degradation rate, which depends on the type and load content, reaching values from 0.006 to 1.270%, in the drop in the adjusted torque per minute of processing. Corn straw had a greater effect on PCL degradation during processing than organophilic clay.

In the present case, a slight increase of the rate of degradation is observed (Table 1) as the clay content or corns straw increases from 0% (neat matrix) to 5%. However, the rates are low and degradation under processing may be disregarded in first approximation. Similar results have been observed in the literature (Reul et al., 2018; Falcão et al., 2017; Almeida et al., 2016).

### 3.2 Differential Scanning Calorimetry (DSC)

Figure 4 shows the plot of heat flow versus time during the cooling and reheating temperature stages for all samples studied.

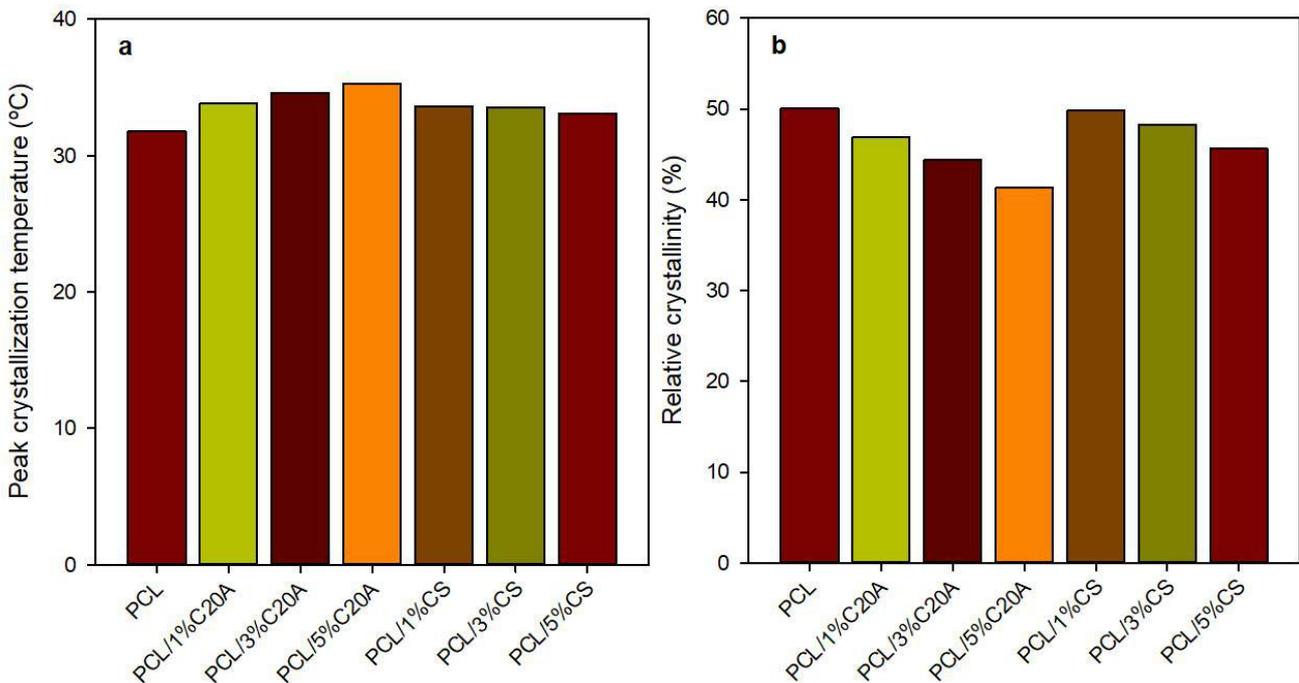
**Figure 4** - Heat flow versus time for neat PCL and C20A and CS composites (exothermic peaks up).



Source: Authors.

In all studied samples single crystallization melting peaks (C1) were observed during the cooling stage. Upon reheating, melting peaks (M2) with well-defined and similar peaks are observed. To determine several transition parameters, crystallization and melting during reheating peaks were analyzed in detail. The first melting was disregarded, to erase the material's thermal history.

**Figure 5** - Peak crystallization temperature (a) and crystallinity (b) for neat PCL and containing 1, 3 and 5% of C20A and CS.

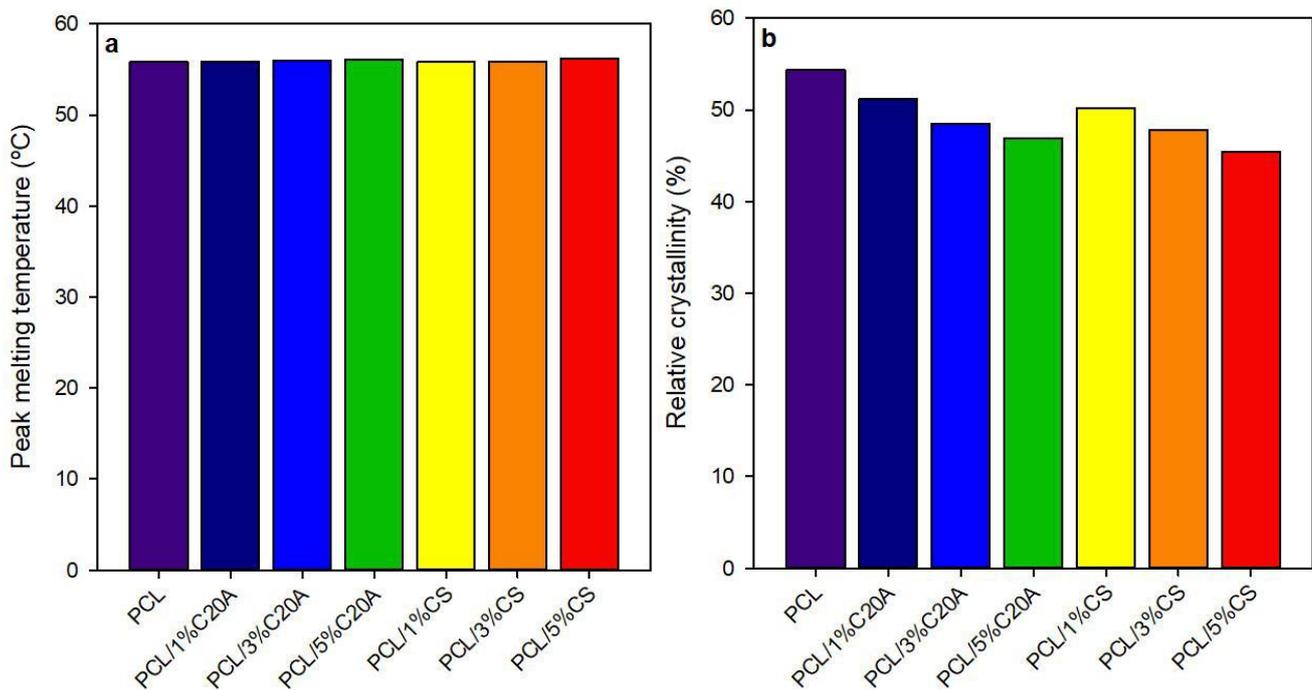


Source: Authors.

Analyzing the obtained data for the crystallization event (C1), the crystallization temperature is independent of the fiber content and filler type for the composites under study. Crystallinity tends to decrease as the content of organophilic clay or fiber in the PCL. The sample with 5% C20A showed a decrease of 17.5% in crystallinity when compared to neat PCL, while the sample with 5% CS showed a decrease of about 9% in its crystallinity. The results indicate that, for this system, the type of filler, particulate or fibrous, did not significantly affect the crystallization temperature or the degree of crystallinity of the systems.

The second melting of all compositions was evaluated separately. Figure 6 illustrates characteristic parameters of the melting event for all samples studied: peak melting temperature and relative crystallinity

**Figure 6** - Peak melting temperature (a) and crystallinity (b) for neat PCL and containing 1, 3 and 5% of C20A and CS.



Source: Authors.

The data show that the melting temperature is independent of the particulate or fibrous filler content. Crystallinity also tends to decrease with filler content, regardless of its neat, and this decrease was greater in compositions with 5% C20A or CS. Comparatively, higher crystallinity values were obtained in systems containing organophilic clay as filler.

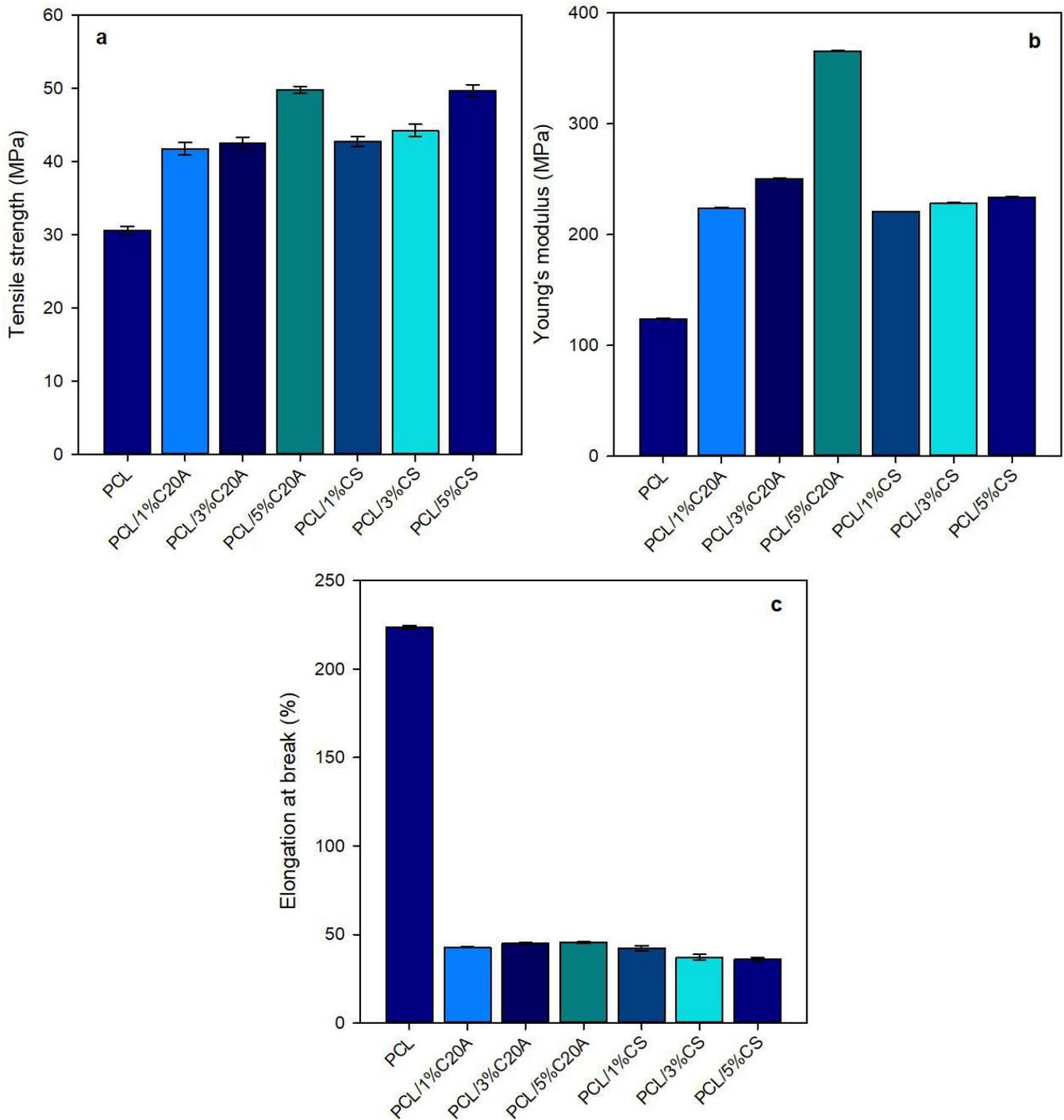
Reul et al. (2017) studied thermal characteristics of polycaprolactone/babassu composites and the results showed that the presence of filler did not significantly affect the temperature of PCL, however, the crystallinity decreased slightly with the filler content, corroborating the results found in this study.

Although the load does not affect the thermal stability of the matrix, the same degrades at lower temperatures than the polymer, resulting in a lower thermal stability of the composite, as seen in the degradation results during processing, torque rheometer parameters during the final processing stage. The decomposition temperature is virtually independent of the type and content of filler.

### 3.3 Tensile Properties

Tensile results for neat PCL and composites are shown in Figure 7.

**Figure 7** - Tensile strength (a) and modulus (b) and elongation at break (c) of neat PCL and C20A and CS composites.



Source: Authors.

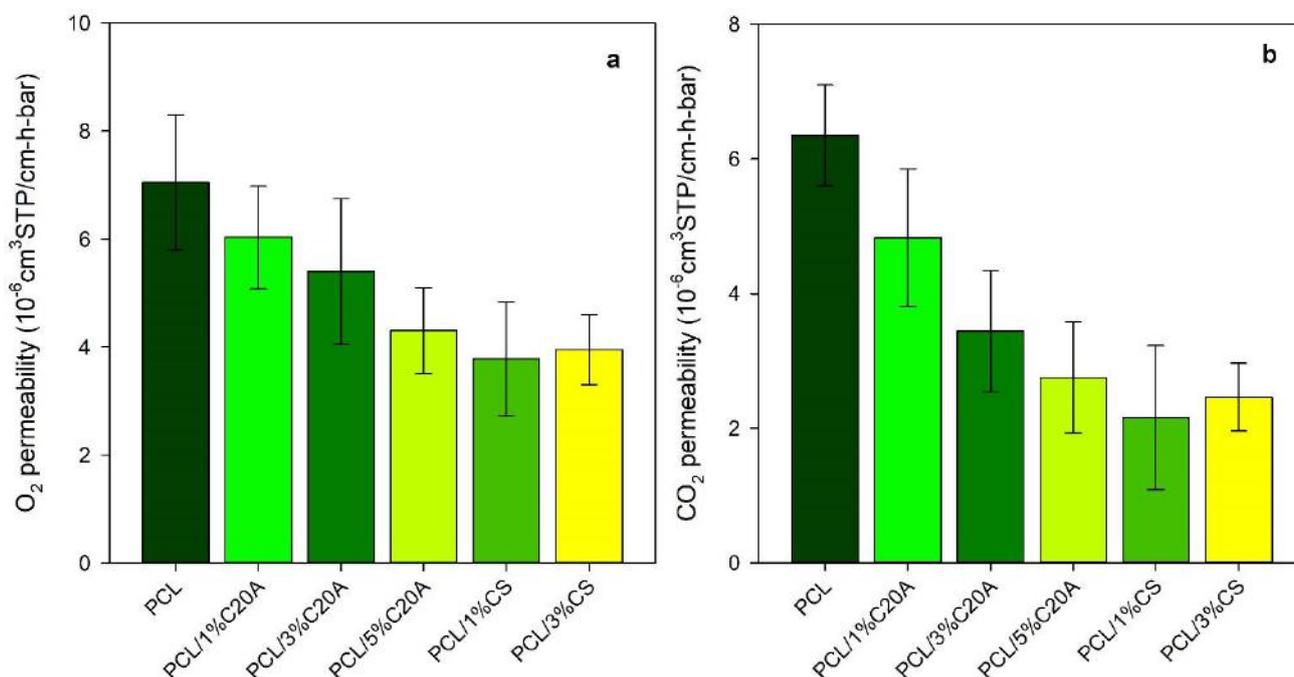
The results indicate that the mechanical properties of the films were affected with the incorporation of clay and vegetal fiber. The tensile strength results show that, for all systems, there was an increase in this property when compared to the neat matrix film, indicating that all the loads used were reinforcing. The tensile modulus of the systems increased with the load content, which was expected, as the loads have a higher elastic modulus than the PCL matrix and act by reducing the free movement of the polymer chains, making movement difficult (Camargo, 2009). The incorporation of the fillers, as expected, reduces the elongation at break of the composites regarding to neat PCL. These reductions were quite significant, proving that the particulate and fibrous loads reduced the ductility of the films, bringing greater stiffness to their structure. The decrease in

elongation at break for films with 5% C20A reached about 80%, and 84% for composites with up to 5% CS. The incorporation of 5% of C20A clay resulted in an increase in modulus of approximately 200% in relation to the matrix. These results suggest that the introduction of the filler stiffened and weakened the PCL films. The incorporation of 5% of CS resulted in an increase of 89% in this property when compared to the neat matrix.

### 3.4 Permeability

Permeability to oxygen and carbon dioxide gases measured at 25°C for the neat PCL and PCL composite films with 1, 3 and 5% C20A and CS is plotted in Figure 8.

**Figure 8** - Permeability to oxygen (a) and carbon dioxide (b) gases of neat PCL and C20A and CS composites.



Source: Authors.

The presence and concentration of inert fillers usually lowers the permeability of films. In present case, the effect the organoclay was very significant: the incorporation 5% C20A in the PCL matrix resulted in a 39% drop of oxygen permeability, and a drop of 57% in carbon dioxide permeability compared to the neat matrix value. However, differently from what was observed for composites with organophilic clay, as the fiber content was increased to 3%, an increase in the permeability of the systems was observed and, for the compositions with 5% of fibers, it was not possible to perform the test. because the films, due to high fragility, broke with the pressure of the gases of the equipment. Addition of organoclay lowers permeability to values comparable to premium packaging films (HDPE, LLDPE), which are much lower than ordinary LDPE film (Krevelen & Nijenhuis, 2009).

Thus, the addition of small amounts of clay results in better and excellent barrier properties. Its presence in the layers of the polymer matrix induces the gases to follow a tortuous path through the polymer, that is, the layered structure of the clay blocks the transmission of gases through the films. Thus, the results indicate that there was a good interaction of the nanofiller with the polymer matrix (PCL), reducing the diffusion of gases through the films. This reduction is related to the increase in the charge/matrix interaction or the dispersion of clay nanoparticles, which are nanofillers impermeable to gases (Falcão et al., 2019).

Regarding the incorporation of fibers in the polymer matrix, it was possible to observe that for the compounds with corn straw, the insertion of 1% of the fiber reduced the oxygen permeability of PCL/CS by 46%. The same occurred with the permeability of PCL films to carbon dioxide. In both cases, the presence of 1% of fibers inside the matrix was quite effective in promoting an increase in the barrier properties of these films. However, as the fiber content was increased to 3%, the permeability of these systems increased, that is, the greater amount of fibers probably generated more defects within the film structure, decreasing its barrier property. This fact can be proven with the insertion of 5% of fibers into the matrix, where it was no longer possible to carry out the permeation test, precisely due to the increase in the fragility of the films that ruptured under the pressure of the gases in the equipment.

It is believed that fiber contents greater than 1% have reduced the barrier properties of the films by increasing the porosity, or number of defects, so that the free volume is now occupied by the diffuser gas, significantly increasing its permeability (Lin and Lu, 2001).

O<sub>2</sub> is the main component that can cause oxidation and that initiates several undesirable changes in foods, such as odor, color, taste and nutrient deterioration. Films providing an adequate oxygen barrier can help improve food quality and extend its shelf life. The concentration of CO<sub>2</sub> is important in specific applications of modified atmosphere packaging. That is, for foods that breathe (fruits and vegetables), it can slow down the metabolism when applied in a certain concentration (Amini & Morrow, 1979).

Films for food packaging applications require, in addition to low crystallinity and low oxygen and carbon dioxide permeability, reasonable mechanical properties. PCL is well known for its excellent properties (high flexibility, impact and tearing resistance) (Reul et al., 2018; Sousa et al.; 2021; Silva et al., 2022). Organoclay composites are reported to improve and preserve these characteristics (Santos et al., 2019; Almeida et al., 2017; Falcão et al., 2019). The data therefore indicate that the compounds under study have efficient barrier properties for possible applications in food packaging and protective coatings, among other applications. The enhanced biodegradability of composite films will be presented in a forthcoming publication.

#### **4. Conclusion**

The data obtained indicate that PCL and PCL/C20A and PCL/CS composites are quite stable and minimally degrade during processing. The incorporation of fillers (clay or fiber) in the films stiffened and weakened the PCL. The presence of the fillers does not significantly affect the thermal stability of the matrix. The addition of small amounts of clay resulted in better and excellent barrier properties in the films studied. The addition of small amounts of C20A and CS to PCL is a useful material alternative that combines the maintenance or improvement of mechanical and thermal properties allied to the excellent barrier properties of the films, having potential application in the packaging industry.

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