Materials Research. 2016; 19(3): 618-627
DOI:http://dx.doi.org/10.1590/1980-5373-MR-2015-0797

Hydrolytic and Thermal Degradation of PCL and PCL/Bentonite Compounds

Danyelle Campos França[a], Elieber Barros Bezerra[a], Dayanne Diniz de Souza Morais[a], Edcleide Maria Araújo[a], Renate Maria Ramos Wellen[b]*

[a]Materials Engineering Department, Federal University of Campina Grande, Campina Grande, PB, 58429-140, Brazil
[B]Materials Engineering Department, Federal University of Paraíba, João Pessoa, PB, 58051-900, Brazil

Received: December 30, 2015; Revised: February 15, 2016; Accepted: March 11, 2016

Poly(Ɛ-caprolactone)/montmorillonite (PCL/MMT) and Poly(Ɛ-caprolactone)/organo-modified montmorillonite (PCL/OMMT) compounds at 3% w/w clay content were prepared by melting mixing. The effect of MMT and OMMT on the degradability of PCL injected specimens was investigated in vacuum at 40ºC for up to 45 days and in aqueous medium at 40ºC for up to 45 days. Selected specimens were collected after 15, 30 and 45 days of exposure. Microstructural changes were monitored during the degradation experiment by means of melt flow rate (MFR), weight loss, X ray diffraction (XRD), mechanical properties, and scanning electron microscopy (SEM). PCL and its compounds revealed not to be prone to hydrolytic degradation with similar results for MFR of samples exposed in vacuum and water. Gain and loss of weight were observed during experiments, probably due to swelling mechanism taking place in two stages, with the amorphous phase being the first to be swelled followed by the crystalline one. By XRD a new peak corresponding to (002) plane was evident for PCL/OMMT. PCL proved to be resistant to degradation since experiments carried out in vacuum or in aqueous medium for up to 45 days were not enough to affect the mechanical integrity of PCL samples.

Keywords: *Poly(Ɛ-caprolactone), Bentonite, Organophilization, Hydrolytic degradation, Thermal degradation, Mechanical properties*

Introduction

Synthetic plastics have been used for various purposes, especially in the packaging industrial sector; however, the majority of these materials constitute at present a serious problem of waste management.

Biodegradable polymers have attracted special attention as a potential solution of this problem, since they can be biologically degraded and therefore can be considered as environmental friendly materials. Among these, a special attention has been given to poly(ε-caprolactone) (PCL),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 -60ºC. [1-4]

PCL has been used in many applications; its biodegradability, biocompatibility and environmental friendliness have contributed to this purpose. It is a prime candidate for use in a variety of disposable materials that are used in food and medical packaging and other consumer items, since plastics disposal is becoming difficult as a result of diminishing landfill space. Its physical properties and commercial availability make it very attractive, not only for specific tools in agriculture for which biodegradation may be required, but also as a substitute of non biodegradable polymers for commodity applications. However, PCL has a low melting temperature (~65°C) and poor thermal and gas barrier properties, which are the main limitations to expand PCL applications to other industrial sectors, such as packaging, in which biodegradability is often sought. These drawbacks could be overcome by dispersion of nanoparticles in PCL to prepare nanocomposites that has proven to be suitable for several applications. [5-10]

In this work PCL/bentonite (PCL/MMT) and PCL/organo-modified bentonite (PCL/OMMT) nanocomposites were processed by melt extrusion followed by injection. Bentonite is natural clay whose main component is the mineral montmorillonite; bentonites are a valuable mineral class for industrial applications because of their high cation exchange capacity and high surface area. However, pristine bentonites contain many impurities, including clay and non-clay minerals as well as organic matter that may interfere with their cation exchange capacity as well as with nano dispersion of the load into the polymer matrices. In their natural form, bentonites are hydrophilic, which may make them difficult to disperse in hydrophobic polymer matrices. In previous work, our research group obtained better clay dispersion results using clay organophilization, a procedure where interlayer inorganic cations are replaced by organic quaternary ammonium cations, to increase the clay interlayer distance and diminish its hydrophilic character, leading to intercalated or exfoliated clay/polymer systems. [11-13]

The main objective of this work is to investigate the degradation behavior of PCL, PCL/MMT and PCL/OMMT compounds in vacuum at 40ºC for up to 45 days and in

*e-mail: wellen.renate@gmail.com

aqueous medium at 40°C for up to 45 days. The effect of degradation conditions into PCL systems was analyzed by means of X ray diffraction (XRD), melt flow rate (MFR), weight loss, mechanical properties, and scanning electron microscopy (SEM).

Experimental

Materials

Poly (Ɛ-caprolactone) – PCL trade name CAPA 6500, with number – average molecular weight $(\overline{M_n})$ = 47500 g/mol (GPC, THF, 25°C) and Intrinsic Viscosity (η) = 2890 Pa.s (70°C, 10 l/s) was purchased from Perstork.

Bentonite Clay trade name Brasgel PA, with cation exchange capacity (CTC) 90 meq/100g was kindly supplied by Bentonit União Nordeste (BUN), Brazil Company. In this work this clay is called MMT.

Methods

Compounding

Masterbatches of 1/1 PCL/clay were made by melt intercalation in a thermokinetic mixer model MH-50H; and ground in a knife mill. The concentrates were diluted to final clay concentration (3% 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. Compounds were oven dried for 24hours at 40°C. Same procedure was applied to neat PCL.

Specimens of PCL, PCL/MMT and PCL/OMMT 3% w/w of clay content for tensile and impact testing according to ASTM D638 and ASTM D256 standards were injection molded in a Fluidmec H 30/40 at 60-70°C.

Bentonite clay organophilization

Bentonite clay, as received was screened and organophilized with quaternary ammonium salt, Praepagen HY - (alkyl dimethyl hydroxyethyl ammonium chloride) following the procedure reported elsewhere. [11-13]

Hydrolytic and thermal degradation

Molded specimens were used in degradation experiments under controlled conditions, i.e. in vacuum at 40°C for up to 45 days and in aqueous medium at 40°C for up to 45 days. Selected specimens were collected after 15, 30 and 45 days of exposure, and their properties evaluated.

Characterization

Torque rheometry

Neat PCL, and PCL /MMT and PCL /OMMT compounds with 3%, 10% and 20% clay 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.

Heat deflection temperature (HDT)

Heat deflection temperature tests carried out in a HDT 6 VICAT P/N 6921.000 instrument (Polymer Laboratory of Federal University of São Carlos – Brazil) according to ASTM D648. Experiments were conducted at load 455kPa, heating rate 120°C/h, specimens were submersed in a silicone bath oil. HDT was determined at 0.25mm of specimen deflection. Presented results are the average of three tests.

Weight loss experiments

Selected specimens were weighted before and after exposure to degradation experiments; changes of weight were computed according to equation:

$$W_L = \frac{W_o - W_f}{W_o} * 100$$

Where: W_o and W_f are specimens weight before and after degradation experiments, respectively.

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 200kgf cell load. Impact tests were carried out in a CEAST Resil-5.5 impact machine operating with a 2.5J pendulum on notched specimens in Izod configuration, according to ASTM D256. Presented results are an average of seven tests.

Melt flow rate

Melt flow rate experiments were performed according to ASTM 1238 in a DSM Plastometer MI-3 at 160°C under a load 2.16 kg; samples were collected after flowing for 10 seconds. Presented results are the average of five tests.

X-ray diffraction (XRD)

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

Scanning electron microscopy (SEM)

Scanning electron microscopy images were acquired in a SSX 550 Superscan–Shimadzu with 15 KV. Fractured surface from mechanical test was covered with gold to avoid accumulation of charges.

Results and Discussion

Organophilization procedure

X-ray diffratograms of bentonite clays, MMT and OMMT, used in this work are shown in Figure 1. The organophilization procedure was successful as the basal distance increased from around 1.31nm to 1.91nm, indicating that the organic cation was incorporated within the clay galleries, possibly increasing the affinity between PCL and OMMT. [11-13]

Thermal stability during processing

Torque rheometry was used to investigate the thermal stability of PCL and PCL/bentonite compounds 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 polymer degradation took place during processing. A constant torque plateau, is an indicative of absence of degradation during polymer processing. [14-16]

Figure 2 shows temperature and torque versus time plots for PCL/bentonite compounds up to 20% w/w clay content. PCL/MMT compounds show constant temperature and torque plateaus for 20 minutes processing time, evidencing absence of molecular weight decaying. PCL/MMT with 20% w/w clay content presented slightly higher torque values, probable due a higher clay content. PCL/OMMT with 20% w/w clay content presented a mild decrease in the torque at constant temperature after 8 minutes of processing, suggesting that degradation reactions took place that may reflect in a drop of PCL molecular weight. It is believed that ammonium salt clay interlayer favored a decreasing in the thermal stability of PCL/OMMT and promoted the degradation. [11]

Among the compositions PCL/MMT and PCL/OMMT analyzed, compounds with 3% w/w clay content were selected for the degradation studies.

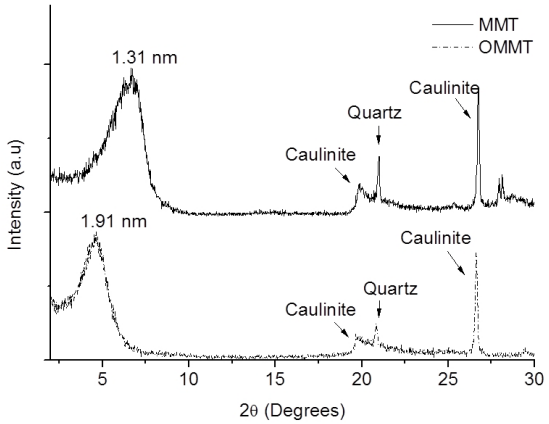

Figure 1. X-Ray diffratograms of MMT and OMMT.

Heat deflection temperature (HDT) measurements

Figure 3 shows HDT results for PCL, PCL/MMT and PCL/OMMT compounds with 3% w/w clay content. HDT of 42.50°C, 53.80°C and 51.45°C, were obtained for these compositions. Upon clay addition PCL keeps its mechanical performance at higher temperatures. This result may be understood as an evidence of affinity and good dispersion of bentonite into PCL matrix (see SEM images in Figure 9), where clay particles interact with PCL macromolecules; these new interactions may support higher stress levels as those applied during HDT experiments. [17,18]

Melt flow rate

Figure 4 shows melt flow rate measurements for PCL, PCL/MMT and PCL/OMMT compounds evaluated during degradation experiments up to 45 days. Figure 4(a) presents the results for tests carried out under vacuum and Figure 4(b) under water, respectively. Mild changes were observed depending on the environment, practically within the experimental error.

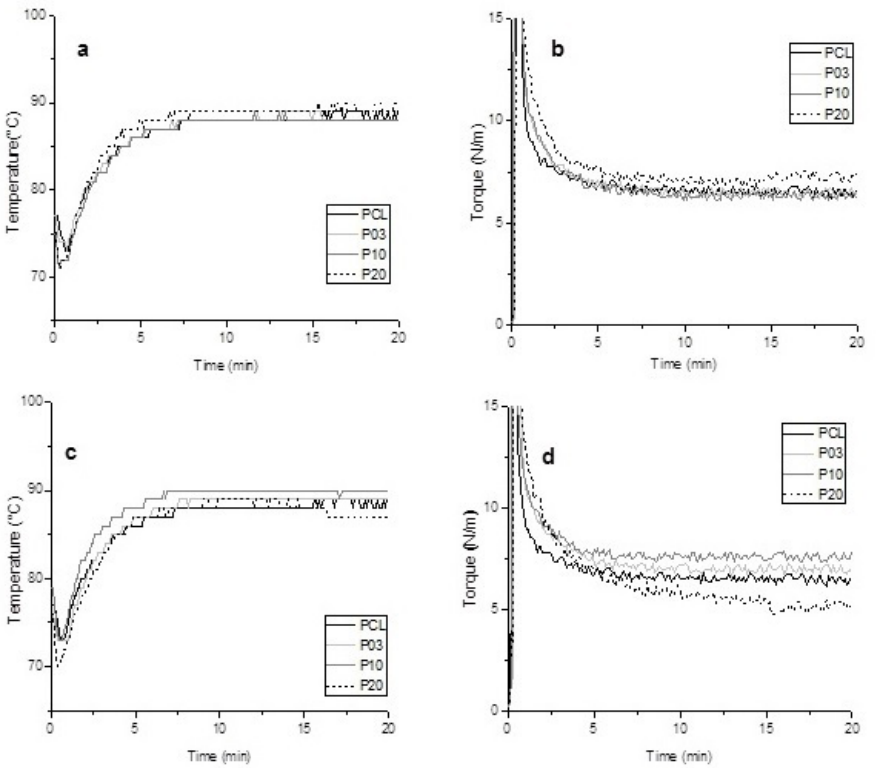

Figure 2. Temperature (left) and torque (right) versus time for PCL/MMT (a) and (b), and for PCL/OMMT (c) and (d), respectively, at several clay content as indicated.

Although PCL is a polyester, it is known from literature not be prone to hydrolytic degradation, this statement may be checked in Figure 4, which shows that tests executed under vacuum and aqueous medium presented very similar results. According to these results, unlike others polyesters as PET and PBT which degrade very fast by hydrolyses reactions, PCL has showed to keep its performance in aqueous medium suggesting that PCL products may be projected for using in humid conditions. [19-23]

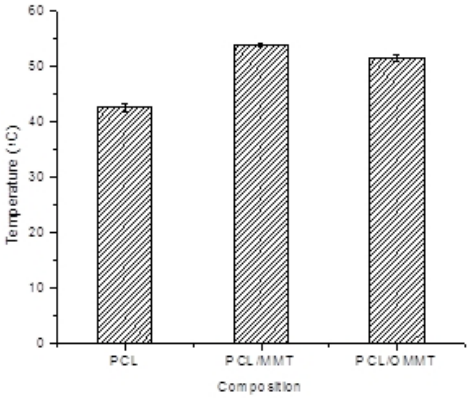

Figure 3. HDT measurements of PCL, PCL/MMT and PCL/OMMT compounds.

Weight loss measurements during degradation experiments

Selected specimens were weighted before and after degradation experiment, and their weight changes computed according to the following equation:

$$W_L = \frac{W_o - W_f}{W_o} * 100$$

Where: W_o and W_f are specimens weight before and after degradation experiments, respectively.

Figure 5 (a) presents results of experiments performed under vacuum and Figure 5 (b) under water.

Specimens subjected to vacuum for 15 days presented W_L values of 0.22%, 0.14% and 0.19% for PCL, PCL/MMT and PCL/OMMT compounds, respectively. After 30 days of exposure W_L values were 0.64%, 0.76% and 0.82%; and for 45 days 0.23%, 0.21% and 0.13%. Results are graphically presented in Figure 5 (a). The highest W_L value took place after 30 days.

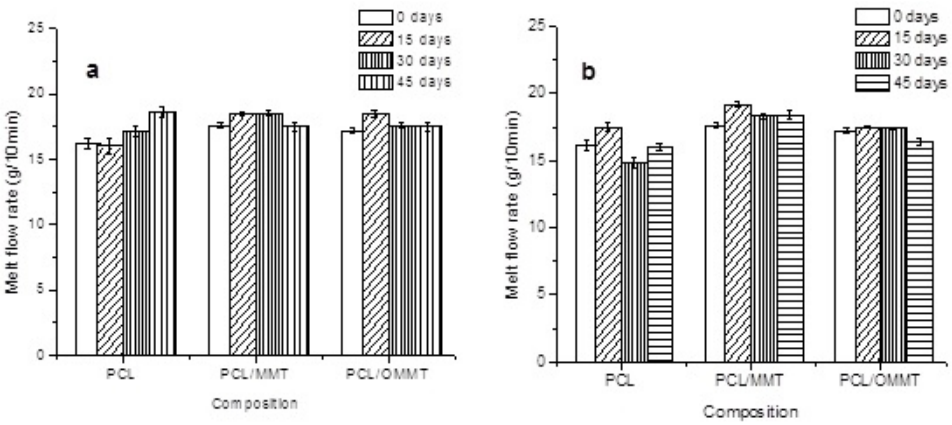

Figure 4. Melt flow rate measurements of PCL, PCL/MMT and PCL/OMMT compounds; under vacuum and temperature (a), under water and temperature (b). (Exposure time indicated).

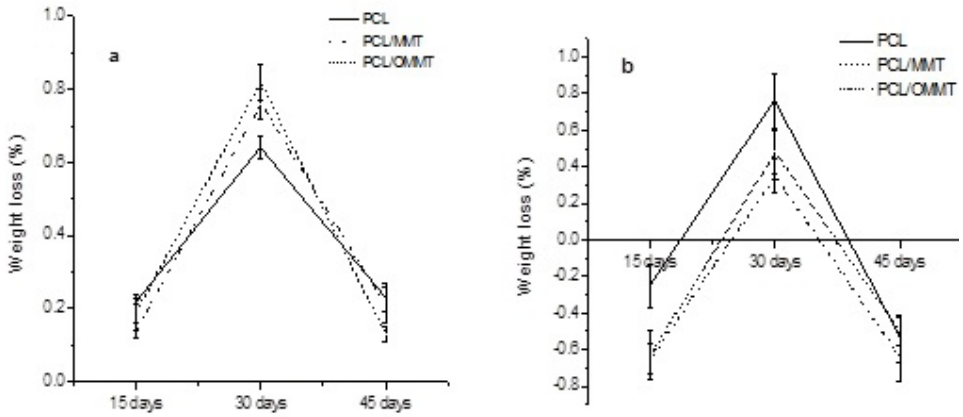

Figure 5. Weight loss during degradation experiments for PCL, PCL/MMT and PCL/OMMT compounds, experiments performed in (a) vacuum and (b) aqueous medium.

Regarding the degradation experiments carried out in aqueous medium at 40ºC, after 15 days was observed an increase in the specimen weight, leading to negative values of W_L; the same trend was observed after 45 day of exposure. The values -0.25%, -0.65% and -0.63%; 0.76%, 0.35% and 0.48%; -0.54%, -0.64% and -0.50% were computed after 15, 30 and 45 days of exposure, for PCL, PCL/MMT and PCL/OMMT, respectively.

The swelling of semi-crystalline polyesters in aqueous media has been reported to occur in two steps: the first step starts with water diffusion into the amorphous regions, which are less organized and allow easier water penetration into the polymer matrix. The second step starts after most of the amorphous regions to be swelled, then the mechanisms proceeds from the edge toward the center of the polymer crystalline domains. [26,27]

In the present work it is possible that, initially, water diffused into the amorphous zones, resulting in negative values for W_L and sample weight increased. Stabilization of the amorphous zone increased W_L, as observed at 30 days of exposure. Advancing with the experiment time, water diffuse into the remaining amorphous and crystalline zones promoting a decrease in W_L, observed after 45 days of exposure. Possibly, for longer times, swelling of the crystalline phase would take place and higher values of W_L would be obtained.

Mechanical Properties

Figure 6 and Tables 1 and 2 display mechanical properties results of neat PCL, PCL/MMT and PCL/OMMT compounds subjected to degradation experiments. In principle, mechanical properties changed little during degradation and

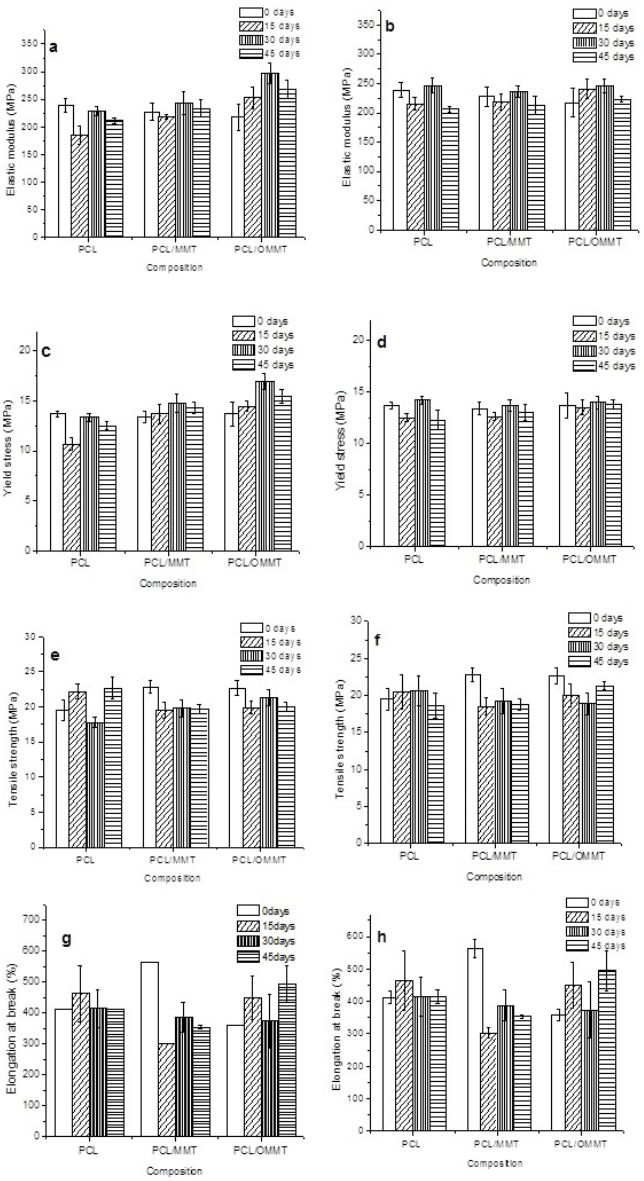

Figure 6. Mechanical properties of PCL, PCL/MMT and PCL/OMMT compounds upon addition of 3% w/w clay content. (a), (c), (e) and (g) specimens exposed to vacuum at 40oC; (b), (d), (f) and (h) specimens immersed in water at 40oC. Degradation time indicated.

Table 1: Mechanical properties of PCL and PCL/MMT and PCL/OMMT compounds subjected into aqueous medium at 40ºC

Specimens subjected into aqueous medium	Elastic modulus (MPa)	Yield stress (MPa)	Tensile strength (MPa)	Elongation at break (%)
PCL	238.8±12.5	13.7±0.3	19.5±1.5	>413.35
PCL 15 days	215.7±11.5	12.5±0.4	20.5±2.3	463.0±91.5
PCL 30 days	247.0±13.4	14.2±0.4	20.7±2.0	414.4±60.6
PCL 45 days	206.2±5.6	12.3±0.9	18.7±1.7	>414.02
PCL/MMT	227.5±16.1	13.4±0.6	22.8±0.9	>563.19
PCL/MMT 15 days	219.4±13.8	12.6±0.4	18.5±1.2	>303.17
PCL/MMT (30 days	237.0±10.0	13.7±0.6	19.3±1.7	387.9±48.0
PCL/MMT 45 days	212.5±16.1	13.0±0.8	18.8±0.8	354.1±5.5
PCL/OMMT	217.4±23.9	13.7±1.2	22.7±1.1	>359.50
PCL/OMMT 15 days	240.8±16.7	13.5±0.7	20.0±1.6	449.1±71.1
PCL/OMMT 30 days	245.5±11.9	14.0±0.6	18.9±1.5	374.0±87.5
PCL/OMMT 45 days	223.2±5.0	13.8±0.4	21.3±0.5	494.4±60.3

Table 2: Mechanical properties of PCL and PCL/MMT and PCL/OMMT compounds subjected into vacuum at 40ºC

Specimens subjected in vacuum	Elastic modulus (MPa)	Yield stress (MPa)	Tensile strength (MPa)	Elongation at break (%)
PCL	238.8±12.5	13.7±0.3	19.5±1.5	>413.35
PCL 15 days	185.3±16.3	10.7±0.6	22.5±1.1	464.0±91.0
PCL 30 days	228.6±9.2	13.4±0.4	17.8±0.7	364.3±22.2
PCL 45 days	211.0±4.8	12.5±0.4	22.7±1.5	507.8±86.2
PCL/MMT	227.5±16.1	13.4±0.6	22.8±0.9	>563.19
PCL/MMT 15 days	218.1±3.3	13.7±1.0	19.5±1.1	321.9±53.4
PCL/MMT 30 days	243.4±21.5	14.8±0.9	19.8±1.2	328.4±97.4
PCL/MMT 45 days	233.6±14.8	14.3±0.6	19.7±0.7	256.9±56.9
PCL/OMMT	217.4±23.9	13.7±1.2	22.7±1.1	>359.5
PCL/OMMT 15 days	252.9±19.8	14.5±0.5	19.9±0.9	234.8±106.7
PCL/OMMT 30 days	297.2±19.0	17.0±0.8	21.3±1.1	191.4±76.2
PCL/OMMT 45 days	268.0±17.5	15.5±0.7	20.0±0.7	255.9±84.7

almost all compositions presented approximately the same values for elastic modulus, yield stress, tensile strength, and elongation at break; neither water nor vacuum experiments showed meaningful changes in mechanical response of the compositions studied in this work.

Regarding to elastic modulus, results are a little higher for vacuum tests compared with those done in aqueous medium. In relation to degradation time, results for 30 days of exposure are higher than those for 15 and 45 days. It is most likely that for 30 days, degradation of the amorphous zones has taken place and the specimens became stiffer; these results agree with Figure 5.

Results for yield strength, Figures 6 c and d (and Tables 1 and 2), for neat PCL are higher under aqueous medium, whereas for PCL/MMT and PCL/OMMT compounds, higher values were obtained in vacuum. Bentonite clay may be abrasive filler, and may interact with PCL macromolecules, probably increasing the hydrolytic degradation.

As PCL melt crystallization ranges from 19ºC to 40ºC, it is possible during degradation experiments at 40ºC, under both conditions, i.e., aqueous medium and vacuum, isothermal crystallization took place promoting an increase on the crystallinity degree and so on the density of the specimens what could have conducted to a higher Elastic Modulus and Yield Strength values. [6,26,28]

Concerning the results of elongation at break, the lowest values were observed for PCL/OMMT compounds. Two effects should be considered in this case, the addition of bentonite to PCL and the organophilization of the clay that could result in a stiffer and brittle compound.

Degradation times investigated in this work weren't long enough to promote considerable changes in the tensile specimens' integrity, as may be visualized in Figure 6. Mechanical properties were almost unchanged after 45 days of exposure.

Impact strength measurements

An interesting behavior occurred during impact experiments. It was impossible to conduct the impact test with the specimens subjected to degradation under vacuum at 40ºC for 30 and 45 days, since they melted during degradation experiment. Probably it was caused due to the lightweight of the impact specimens that is approximately 2.5 g whereas the tensile specimen´s weight is approximately 10 g. This result should be taken as a warning: PCL may melt at temperature as low as 40ºC. On the other hand, all specimens immersed in water at 40ºC, did not melt and impact test were executed for 15, 30 and 45 day of exposure. Figure 7 and Tables 3 and 4 show the collected data from impact tests.

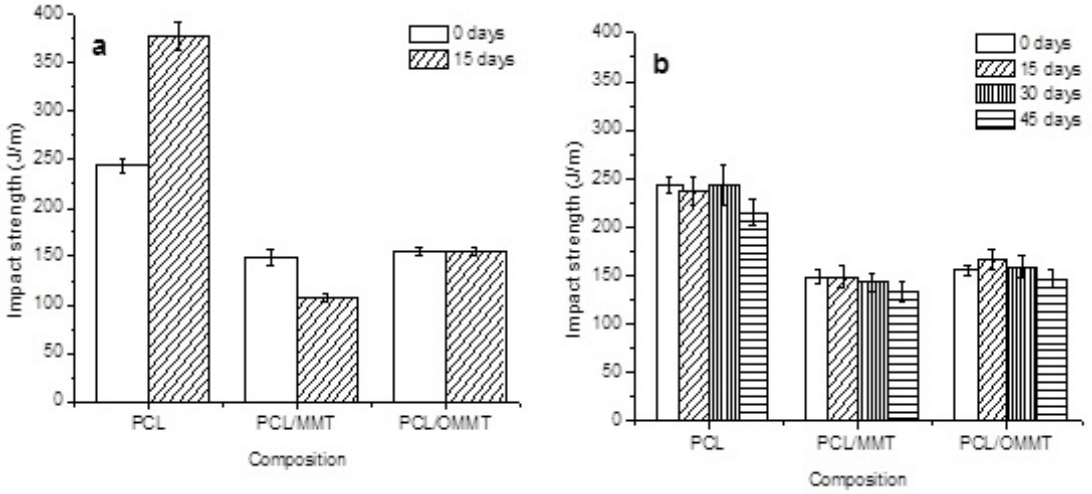

Figure 7. Impact strength of PCL, PCL/MMT and PCL/OMMT compounds upon addition of 3% w/w clay. (a) Specimens exposed to vacuum at 40oC; (b) specimens immersed in water at 40oC. Degradation time indicated.

Table 3: Impact strength of PCL and PCL/MMT and PCL/OMMT compounds subjected into aqueous medium at 40°C

Specimens subjected in water	Impact strength (J/m)			
	0 days	15 days	30 days	45 days
PCL	243.6±7.6	237.0±14.0	243.0±20.3	215.1±13.9
PCL/MMT	148.6±7.7	148.9±11.9	143.8±9.3	133.3±10.9
PCL/OMMT	155.3±4.6	167.1±10.1	159.2±11.3	146.6±9.2

Table 4: Impact strength of PCL and PCL/MMT and PCL/OMMT compounds subjected into vacuum at 40°C

Specimens in vacuum	Impact strength (J/m)	
	0 days	15 days
PCL	243.6±7.6	377.8±13.9
PCL/MMT	148.6±7.7	107.3±3.9
PCL/OMMT	155.3±4.6	71.3±3.9

A different behavior was verified for neat PCL after 15 exposure days: under vacuum, it presented very high value of impact strength while compounds with MMT and OMMT presented lower results; we have not found a plausible explication for it.

In general impact strength of PCL/MMT and PCL/OMMT compounds was lower than neat PCL; bentonite clay particles may be acted as stress concentrator inside the PCL matrix and decreased the impact response.

X ray diffraction (XRD) measurements

The study of the effect of degradation on the crystalline phase of PCL and its compounds with bentonite clay was performed by means of XRD. Figure 8 presents X ray diffratograms of PCL, PCL/MMT and PCL/OMMT compounds subjected to degradation experiments.

XRD tests performed with degraded specimens under vacuum or in water did not present significant changes in the XRD peaks. This result may be interpreted as the absence of PLC intercalation in the interlayer spacing of the clay. Degradation did not cause major changes in the crystalline character of PCL, whereas all diffratograms peaks were observed around 21,1° and 23,5° corresponding to basal distance 0.42 nm and 0.38 nm due to 110 and 200 planes.

For PCL/OMMT compounds degraded in water, the increase of basal distance (d_{001}) was more pronounced for 45 days (d_{001}=2.84 – 3.11nm); and a new peak corresponding to a (002) plane with d_{002}=1.56 – 1.64nm was observed after 15 exposure days. [24-27]

Scanning Electron Microscopy (SEM) Images

SEM images of fractured surface of PCL and PCL/MMT compounds, non-degraded and immersed in water for 45 days, acquired during impact test, are presented in Figure 9. These surfaces were covered with gold to avoid accumulation of charges.

Figure 9 (a) shows SEM image of non-degraded PCL, a ductile fracture with plastic deformation may be observed. Regarding to the effect of degradation on the PCL microstructure none significant modification is verified by SEM, seeing that ductile fracture and plastic deformation is evinced as illustrated in Figure 9 (b). It is worth mentioning

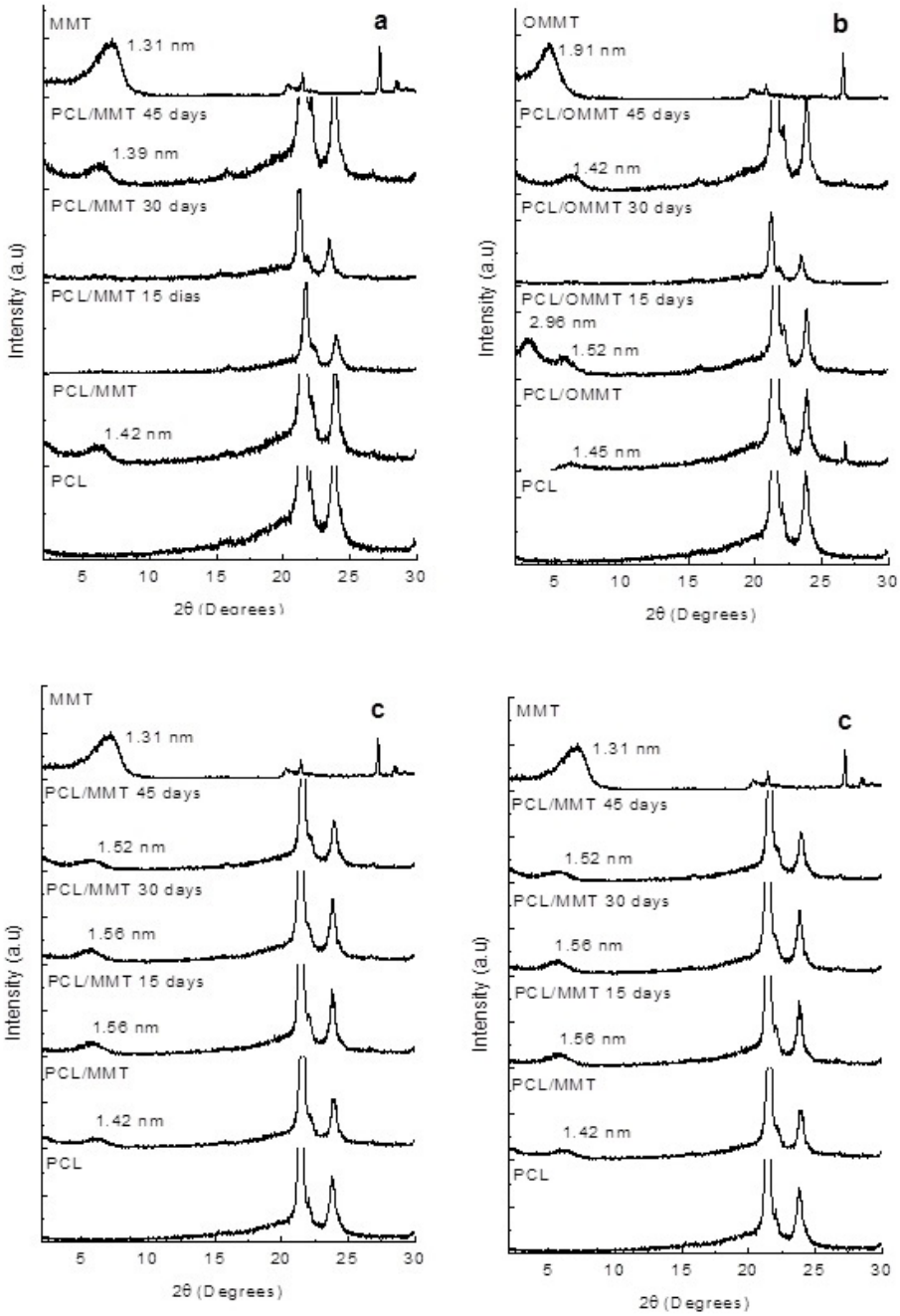

Figure 8. X ray diffratograms of MMT, OMMT, PCL, PCL/MMT and PCL/OMMT compounds. (a) and (b) tests executed with specimens subjected to vacuum at 40oC, (c) and (d) specimens immersed in aqueous medium at 40oC. Degradation time indicated.

these experiments were done in ambient temperature (~ 23°C), this temperature is high enough to allow macromolecular movements and to promote the development of PCL rubbery phase that probably conducted to the plastic deformation observed in Figure 9 (a) and (b).

In Figure 9 (c) MMT particles are clearly seen, some of them seem to be detached from PCL matrix, a ductile fracture is also observed, however, less plastic deformation is observed in relation to neat PCL, this aspect agrees with the lowest values of impact strength obtained for the compounds with bentonite (Figure 7). In Figure 9 (d) thin fibrils are observed what may be evidences that degradation mechanisms have taken place. Similar SEM images were captured for PCL/OMMT compounds, images not showed here.

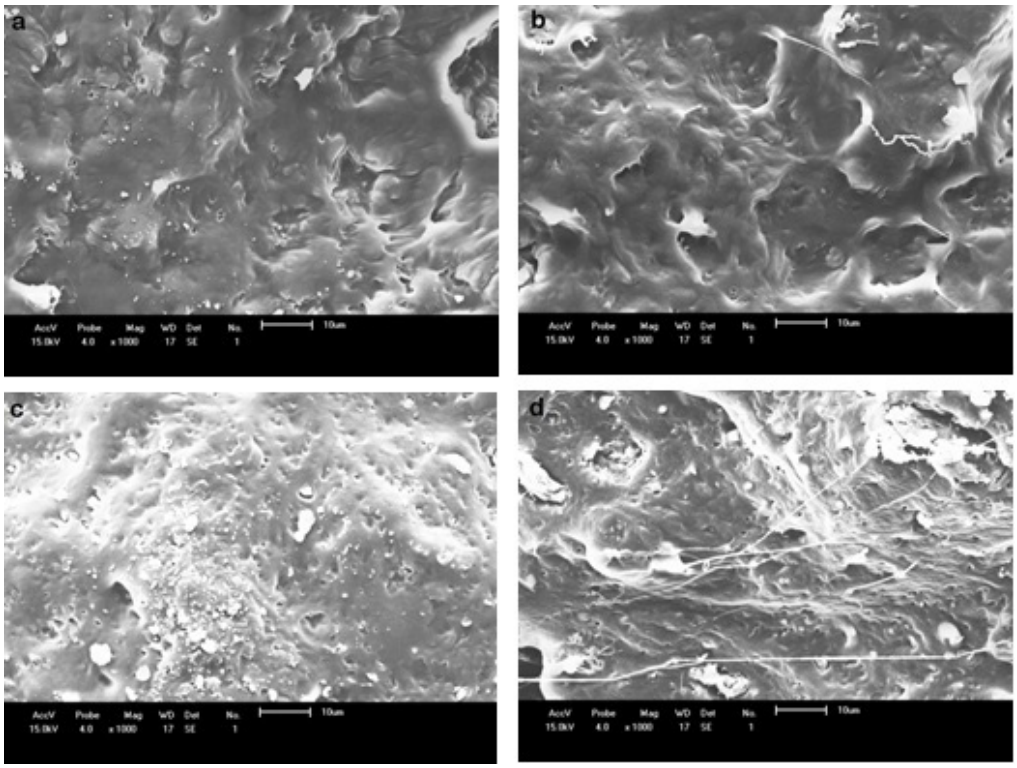

Figure 9. SEM images of PCL non-degraded (a), PCL immersed in water for 45 days of exposure (b), PCL/MMT non-degraded (c), PCL/MMT immersed in water for 45 days of exposure (d).

Conclusions

Adding bentonite to PCL increased its thermal stability by 26% and 21% as observed for HDT experiments of PCL/MMT and PCL/OMMT, respectively. PCL and its compounds were verified not to be prone to hydrolytic degradation, MFR tests showed similar results in vacuum and water after 45 days of exposure. PCL immersed in water for 45 days presented a swelling process in two stages, probably; first amorphous zones are swelled at 15 days of exposure followed by the crystallines ones at 45 days. According to XRD diffratograms, neither addition of bentonite nor degradation experiments changed the crystalline character of PCL. Bentonite was observed to be well dispersed in PCL matrix by SEM images, a ductile fracture with plastic deformation was also observed for neat PCL and its compounds. Impact specimens subjected to degradation experiments in vacuum at 40°C melted, what may be linked to their lightweight (2.5 g). Degradation experiments performed with thick tensile specimens (10 g) for 45 days in vacuum or in aqueous medium at 40°C were not enough to affect the mechanical integrity of PCL specimens what is a good result since PCL products may be used in these drastic conditions with no damage.

Acknowledgments

The authors are indebted to CNPq and Capes (Brasilia/DF, Brazil) for the financial support; to Bentonit União Nordeste for supplying the clay and to Federal University of São Carlos, Polymer Laboratory for HDT experiments.

References

1. Rosa DS, Chui QS, Pantano Filho R, Agnelli JA. Avaliação da biodegradação de poli-β-(Hidroxibutirato), poli-β-(hidroxibutirato-co-valeraro) e poli-β-(caprolactona) em solo compostado. *Polímeros: Ciências e Tecnologia.* 2002;12(4):311-317. doi: 10.1590/S0104-14282002000400015
2. Bucci DZ, Tavares LB, Sell I. PHB packaging for the storage of food products. *Polymer Testing*. 2005;24:564-571.
3. Falcone DM, Agnelli JÁ, Faria LI. Panorama setorial e perspectivas na área de polímeros biodegradáveis. *Polímeros: Ciências e Tecnologia.* 2007;17(1):5-9. doi: 10.1590/S0104-14282007000100005
4. Harding KG, Dennis JS, von Blottnitz H, Harrison ST. Environmental analysis of plastic production processes: Comparing petroleum-based polypropylene and polyethylene with biologically-based poly-ß-hydroxybutyric acid using life cycle analysis. *Journal of Biotechnology.* 2007;130(1):57-66. doi:10.1016/j.jbiotec.2007.02.012
5. Fukushima K, Abbate C, Tabuani D, Gennari M, Rizzarelli P, Camino G. Biodegradation trend of poly(ε-caprolactone) and nanocomposites. *Materials Science and Engineering C.* 2010;30(4):566-574. doi:10.1016/j.msec.2010.02.012
6. Renstad R, Karlsson S, Albertsson AC, Werner PE, Westdah M. Influence of processing parameters on the mass crystallinity

of poly(3-hydroxybutyrate- co-3-hydroxyvalerate). *Polymer International*. 1997;43(3):201-209.

7. Lam C, Teoh SH, Hutmacher DW. Comparison of the degradation of polycaprolactone and polycaprolactone–(β-tricalcium phosphate) scaffolds in alkaline medium. *Polymer International.* 2007;56(6):718–728. doi: 10.1002/pi.2195
8. Lepoittevin B, Devalckenaere M, Pantoustier N, Alexandre M, Kubies D, Calberg C, et al. Poly (Ɛ-caprolactone)/ clay nanocomposites prepared by melt intercalation: mechanical, thermal and rheological properties. *Polymer*. 2002;43(14):4017-4023.
9. Sinha R, Okamoto M. Polymer/Layered silicate nanocompósitos: a review from preparation to processing. *Progress in Polymer Science.* 2005;28:1539-1641.
10. Lotto NT, Calil MR, Guedes CG, Rosa DS. The effect of temperature on the biodegradation test. *Materials Science and Engineering C.* 2004;24(5):659-662.
11. Barbosa R. *Estudo da modificação de argilas bentoníticas para aplicação em nanocompósitos de polietileno* [tese]. Campina Grande, Paraíba: Universidade Federal de Campina Grande; 2009.
12. Araújo EM, Barbosa R, Morais CR, Melo TJ, Souza AG. The effects of organoclays on the thermal processing of PE/Clay nanocomposites. *Journal of Thermal Analysis and Calorimetric*. 2007;90(3):841-848.
13. Morais DD, Barbosa R, Medeiros KM, Araújo EM, Melo TJ. Preparation of poly(lactic acid)/bentonite clay bio-nanocomposite. *Materials Science Forum*. 2014;775-776:233-237. doi: 10.4028/www.scientific.net/MSF.775-776.233
14. Lyons JG, Holehonnur H, Devine DM, Kennedy JE, Geever LM, Blackie P, Higginbotham C. The incorporation of an organically modified layered silicate in monolithic polymeric matrices produced using hot melt extrusion. *Materials Chemistry and Physics*. 2007;103(2):419-426.
15. Mould S, Barbas J, Machado AV, Nóbrega JM, Covas JA. Measuring the rheological properties of polymer melts with on-line rotational rheometry. *Polymer Testing*. 2011;30(6):602-610. doi:10.1016/j.polymertesting.2011.05.002
16. Aho J, Boetker JP, Baldursdottir S, Rantanen J. Rheology as a tool for evaluation of melt processability of innovative dosage forms. *International Journal of Pharmaceutics*. 2015;494(2):623-642. doi:10.1016/j.ijpharm.2015.02.009
17. Wong AC. Heat deflection characteristics of polypropylene and polypropylene/polyethylene binary systems. *Composites Part B: Engineering;* 2003;34(2):199-208. doi:10.1016/S1359-8368(02)00080-X
18. Bledzki A, Mamun AA, Feldmann M. Polyoxymethylene composites with natural and cellulose fibres: Toughness and heat deflection temperature. *Composites Science and Technology.* 2012;72(15):1870-1874. doi:10.1016/j.compscitech.2012.08.004
19. Rodenas-Rochina J, Vidaurre A, Cortázar IC, Lebourg M. Effects of hydroxyapatite filler on long-term hydrolytic degradation of PLLA/PCL porous scaffolds. *Polymer Degradation Stability*. 2015;119:121-131. doi:10.1016/j.polymdegradstab.2015.04.015
20. Castilla-Cortázar I, Más-Estellés J, Meseguer-Dueñas JM, Escobar Ivirico JL, Vidaurre A. Hydrolytic and enzymatic degradation of a poly(ε-caprolactone) network. *Polymer Degradation Stability.* 2012;97(8):1241-1248. doi:10.1016/j.polymdegradstab.2012.05.038
21. Larrañaga A, Aldazabal P, Martin FJ, Sarasua JR. Hydrolytic degradation and bioactivity of lactide and caprolactone based sponge-like scaffolds loaded with bioactive glass particles. *Polymer Degradation Stability.* 2014;110:121-128. doi:10.1016/j.polymdegradstab.2014.08.021
22. Zhang L. Kinetics of hydrolysis of poly(ethylene terephthalate) wastes catalyzed by dual functional phase transfer catalyst: A mechanism of chain-end scission. *European Polymer Journal.* 2014;60:1-5. doi:10.1016/j.eurpolymj.2014.08.007
23. Lavilla C, Muñoz-Guerra S. Biodegradation and hydrolytic degradation of poly(butylene terephthalate) copolyesters containing cyclic sugar units. *Polymer Degradation and Stability*. 2012;97(9):1762-1771. doi:10.1016/j.polymdegradstab.2012.06.008
24. Khoee S, Kardani M. Preparation of PCL/PEG superporous hydrogel containing drug-loaded nanoparticles: The effect of hydrophobic-hydrophilic interface on the physical properties. *European Polymer Journal.* 2014;58:180-190. doi:10.1016/j.eurpolymj.2014.06.024
25. Kaunisto E, Marucci M, Borgquist P, Axelsson A. Mechanistic modelling of drug release from polymer-coated and swelling and dissolving polymer matrix systems. *International Journal of Pharmaceutics*. 2011;418(1):54-71. doi:10.1016/j.ijpharm.2011.01.021
26. Jiang S, Ji X, An L, Jiang B. Crystallization behavior of PCL in hybrid confined environment. *Polymer*. 2001;42:3901-3907.
27. Vertuccio L, Gorrasi G, Sorrentino A, Vittoria V. Nano clay reinforced PCL/starch blends obtained by high energy ball milling. *Carbohydrate Polymers*. 2009;75(1):172-179. doi:10.1016/j.carbpol.2008.07.020
28. Wellen RM, Rabello MS. The kinetics of isothermal cold crystallization and tensile properties of poly(ethylene terephthalate). *Journal of Materials Science.* 2005;40:6099-6104.