

Poly(ϵ -caprolactone) Degradation Under Acidic and Alkaline Conditions

Aurelio Ramírez Hernández*, Oscar Crisanto Contreras, Jorge Conde Acevedo,
Leticia Guadalupe Navarro Moreno

Campus Tuxtepec, Circuit Central #200, Col. Park Industrial, University of Papaloapan, Tuxtepec, C.P. 68301, Oaxaca, México

Abstract In this paper, the chemical degradation of poly(ϵ -caprolactone) by hydrolysis was carried out. Poly(ϵ -caprolactone) was successfully synthesized via the ring-opening polymerization of ϵ -caprolactone at 155°C with ammonium heptamolybdate. Poly(ϵ -caprolactone) was characterized by Fourier Transform Infrared Spectroscopy. The hydrolyses were carried out under acid and alkaline conditions using HCl, H₂SO₄, NaOH, and KOH. The temperature used in the hydrolyses ranged from 40°C to 140°C, while the solution concentrations, time, and the mass of the samples during the chemical degradation were held constant. Under these degradation conditions a loss of weight of poly(ϵ -caprolactone) was observed when the temperature was increased. For example, for 30 minutes of degradation using sulfuric acid at temperatures of 120°C and 140°C, the poly(ϵ -caprolactone) was degraded 25.00% and 36.31% respectively. The alkaline hydrolysis process is more rapid than acid hydrolysis. For example, after 30 minutes in NaOH at temperatures of 120°C and 140°C, the poly(ϵ -caprolactone) was degraded 94.60% and 100%, respectively.

Keywords Degradation, Biodegradable, Poly(ϵ -caprolactone), Acid and Alkaline Hydrolysis

1. Introduction

Polymers are currently produced in large quantities in order to improve the quality of life for many people, and also polymers let contribute to the development of science and technology. But one major disadvantage of products elaborated with synthetic polymers is the negative effect on the environment when they are thrown out. For this reason, biodegradable polymers are being produced in laboratories [1-3], such is the case of poly(ϵ -caprolactone) (PCL), which is a semi-crystalline thermoplastic polyester [4-5]. PCL is synthesized by the ring opening polymerization (ROP) of ϵ -caprolactone (ϵ -CL), it is composed of five methylenes [(CH₂)₅] and an ester functional group [CO₂] as the repeating unit. PCL and its derivatives are polymers that have been of great interest in the pharmaceutical industry as matrices for medical formulas, for this reason, PCL is used in therapeutic medicine due to its high permeability and low toxicity. Another one of the applications of PCL is in the production of degradable plastic bags. The ester functional group of PCL tends to be hydrolyzed and fragmented into short polymeric chains with low molecular weight. It has been reported that PCL is degraded by microorganisms, enzymes, and also chemical degradation methods (hydrolysis) [6-10].

In the case of the chemical methods, questions arise: Which is faster: the degradation of PCL in acidic or alkaline conditions? how can the degradation process be described?

In this paper, an evaluation and comparison of the chemical methods for PCL degradation using acidic and alkaline hydrolysis is carried out.

2. Description of Experiment

2.1. Equipment

- IKA RCT basic electric hot plate with magnetic stirrer.
- Reflux water system.
- Perkin-Elmer spectrum 100 FT-IR spectrometer.
- Thermo Scientific vacuum pump.
- ¹H-NMR: Varian Gemini 2000 and Varian unity Plus 300.

2.2. Reactants

- ϵ -Caprolactone 99% (Sigma Aldrich).
- Ammonium heptamolybdate tetrahydrated (Riedel-de Haën).
- Anhydrous methanol 99.85% (Baker).
- Chloroform 99.97% (Golden Bell).
- Hydrochloric acid 37.8% (Chemical Meyer).
- Sulfuric acid 98.4% (Baker Analyzed).
- Potassium hydroxide 86.03% (Chemical Meyer).
- Sodium hydroxide 98.2% (Golden Bell).

2.3. Methods

* Corresponding author:

chino_raha@hotmail.com (Aurelio Ramírez Hernández)

Published online at <http://journal.sapub.org/ajps>

Copyright © 2013 Scientific & Academic Publishing. All Rights Reserved

2.3.1. PCL synthesis

Sixty millimeters of ϵ -caprolactone, 0.3ml of water and 33mg of ammonium heptamolybdate were placed a 100ml around bottom flask, which was set up in a reflux system for 120 minutes at 155°C. The mixture was stirred at 250 rpm (see Figure 1).

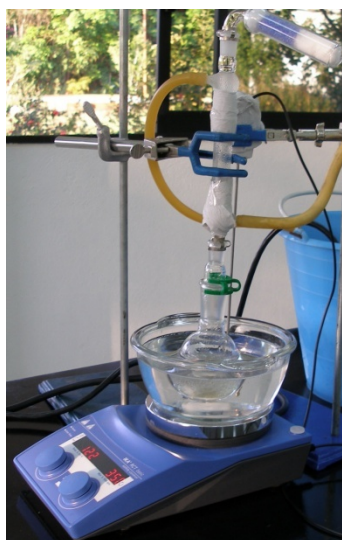


Figure 1. PCL synthesis process

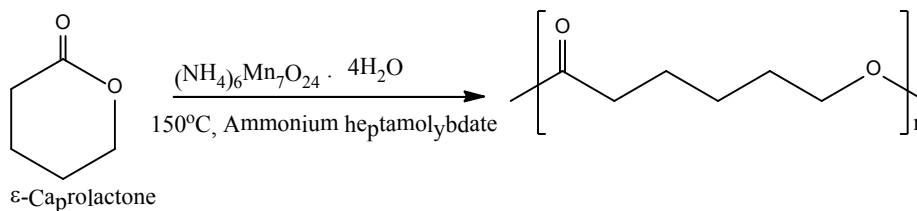


Figure 2. Synthesis of poly(ϵ -caprolactone) (PCL)

The obtained PCL was purified by dissolution into chloroform and precipitation with methanol, finally being isolated by vacuum filtration.

2.3.2. PCL Degradation

The mixture of 2.5g PCL and 30ml acid or alkaline solution was placed in a 50ml round bottom flask and set up to reflux for 30 minutes. The solution was stirred at 250rpm. The degradation temperature interval was 40°C to 140°C. The percent of non-degraded PCL was determined using the equation:

$$\% \text{ of non - degraded PCL} = \frac{\text{final mass of PCL}}{\text{Initial mass of PCL}} \times 100[1]$$

2.3.3. PCL Characterization

The characterization of PCL and non-degraded PCL was by Fourier Transform Infrared Spectroscopy (FT-IR) and Nuclear Magnetic Resonance (NMR) spectroscopy.

3. Results and Discussion

3.1. PCL Synthesis

PCL was synthesized from the polymerization of ϵ -caprolactone using ammonium heptamolybdate as a catalyst at 155°C (see Figure 2).

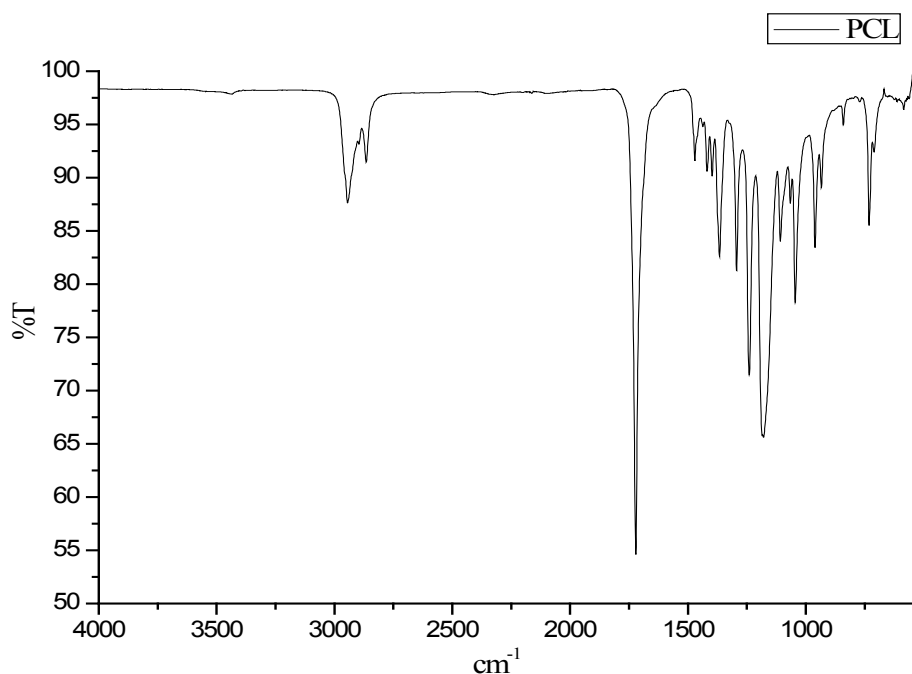


Figure 3. FT-IR Spectrum of PCL

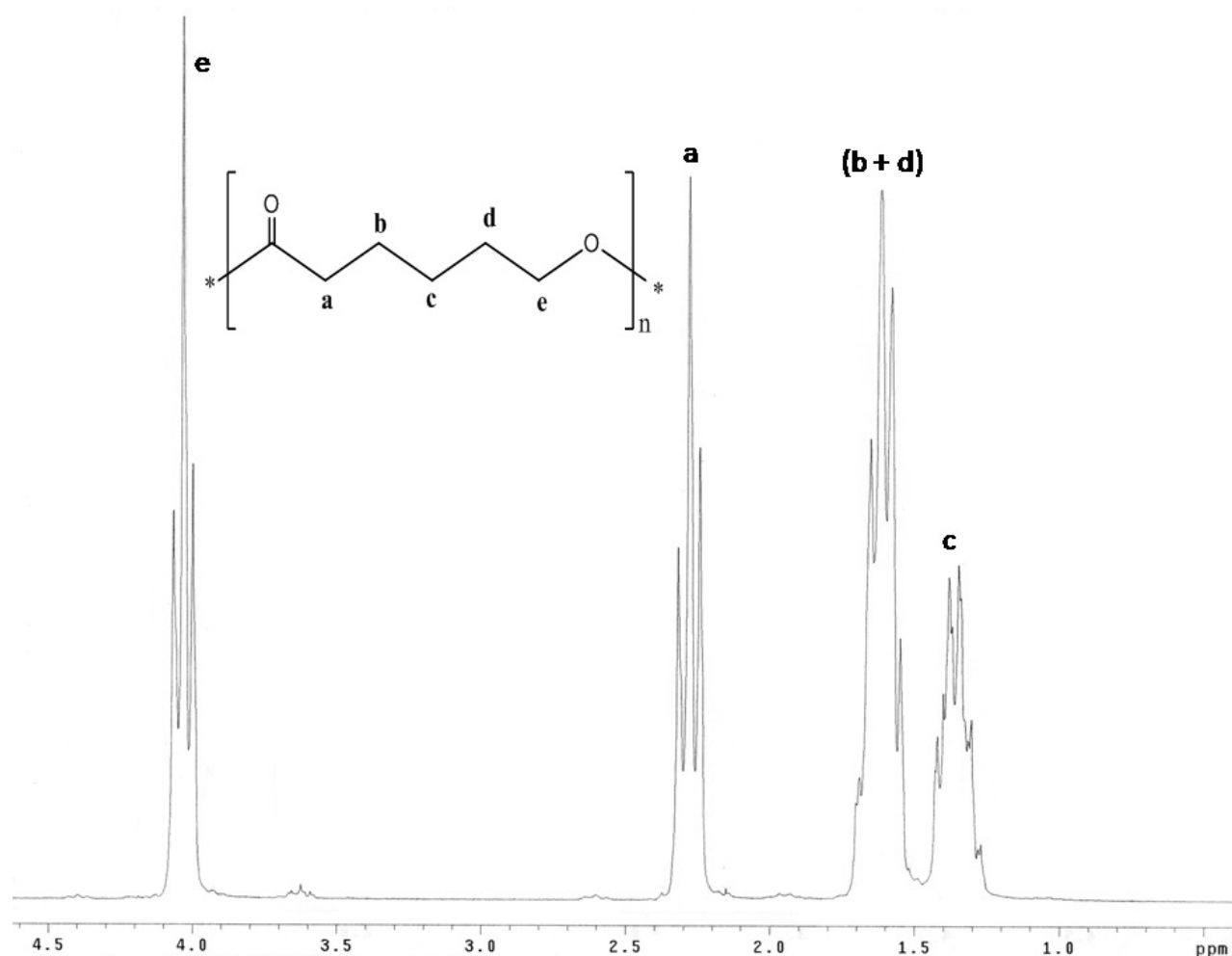


Figure 4. Nuclear Magnetic Resonance spectrum (¹H NMR) of PCL

In Figure 3, in the FT-IR spectrum of PCL weak signals can be observed at 2944.17 and 2865.08 cm⁻¹ which correspond to asymmetric elongation of the methylene-oxygen (CH₂-O) and symmetric elongation of the methylene groups (CH₂-), respectively.

Intense signal that is characteristic of the carbonyl can be observed at 1721.23 cm⁻¹, and belongs to the aliphatic ester (CO₂-) of the PCL. The signal at 1470.92 cm⁻¹ corresponds to the asymmetric elongation of the carbon-hydrogen (C-H) of the methylene, and, the signal at 731.52 cm⁻¹ corresponds to the scissors-like bending motion of the methylene. It is also possible to observe the characteristic signals of the PCL polymer in the spanning 1470.92 to 731.52 cm⁻¹, which correspond to the deformation of the methylene groups (CH₂-).

In Figure 4, the obtained proton nuclear magnetic resonance (¹H NMR) spectrum of the PCL is shown, in this spectrum it is possible to observe the signal at 1.3 ppm (c) which corresponds to methylene (-CH₂-); This signal reveals to us that the structure of the PCL polymer still remains.

At around 1.7 - 1.5 ppm (b+d), it is possible to observe signals that correspond to overlapped methylene. The signal at 2.3 ppm (a) is generated by methylene and it is displaced due to the influence of neighbor atoms, for instance,

carbonyl (C=O) and a methylene (-CH₂-). At 4 ppm (e) it is possible to observe the signal of the methylene (-CH₂-O).

3.2. PCL Degradation

In Table 1, we present the mass percentages of the PCL that were obtained by using equation [1] after the degradation processes, the solutions that were used for each degradation process are also specified in Table 1.

Table 1. Mass percentage of PCL

| Temp. (°C) | Obtained mass of PCL for four different acid and base solutions (4M) | | | |
|---------------|---|--------------------------------|--------|--------|
| | HCl | H ₂ SO ₄ | NaOH | KOH |
| 40 | 2.4005 | 2.6889 | 1.5110 | 1.1973 |
| 60 | 2.4480 | 2.5862 | 0.5761 | 1.2688 |
| 80 | 2.2934 | 2.5205 | 0.9527 | 1.4884 |
| 100 | 2.3583 | 2.4814 | 0.8840 | 1.5479 |
| 120 | 1.6573 | 1.8765 | 0.1348 | 0.0219 |
| 140 | 1.3022 | 1.5922 | 0 | 0.7598 |

Also, it is possible to observe in Table 1 that the mass percentage of PCL decreases as temperature is increased, but we realize that there is likely no trend in the data as a result of the physical interaction between methanol and non-degraded PCL.

Based on the results of Table 1, we made a comparison between the degradation processes that were carried out with both acid solutions, hydrochloric acid (HCl) and sulfuric acid (H₂SO₄). The result is that the more suitable solution for degradation of PCL is hydrochloric acid HCl, this is due to the degradation process being faster for monoprotic acids than for polyprotic acids. On the other hand, the results of the comparison between the degradation processes with both base solutions, sodium hydroxide (NaOH) and potassium hydroxide (KOH), suggest that the more suitable solution for PCL degradation is NaOH. This is probably due to the higher electronegativity of the hydroxyl (OH) group present in each one of the base solutions. From the comparison between acid and base solutions we can establish that for PCL degradation, base solutions present some advantages over acid solutions. That is to say, the carbonyl group of the PCL is a very reactive zone that is favorable for the nucleophilic attack of the base solutions. It is important to mention that probably the ester group (CO₂) of the repeating unit of the PCL polymer tends to be hydrolyzed. In consequence, the polymeric chain tends to fragment itself resulting in similar oligomers of low molecular weight.

The Figure 5 presents an example of the fragmentation of poly(ethylene terephthalate) (PET).

A photograph of non-degraded PCL is shown in Figure 6, this picture was obtained during the degradation process after PCL was purified by a precipitation process using chloroform and methanol, followed by vacuum filtration.

In Figure 7, a comparison between the FT-IR spectrums of synthesized PCL (continuous line) and non-degraded PCL (discontinuous line) is shown. Two of the main differences between the spectra are that at 3407.29 cm⁻¹, the elongation signal of the hydroxyl of the carboxylic acid (O-H) is

observed only in the spectrum of the non-degraded PCL; this signal is accentuated due to the presence of low molecular weight oligomers. These oligomers present signals in the interval 3747.66 to 3002.63 cm⁻¹. The second difference is the intensity of the signals in the interval 2944.24 to 2865.84 cm⁻¹, that corresponds to the methylene groups. Signal intensities are higher for the non-degraded PCL. At 1721.89 cm⁻¹ there is a slight displacement, which results from the presence of carbonyl acid.

The highest intensity signal is due to the abundant proportion of the carbonyl (acid [CO₂-]) in relation to that of the PCL (see Figure 3). The differences between both FT-IR spectra confirm degradation of PCL.

Also, it is possible to observe that in the interval of 1607.64–901.68 cm⁻¹, there is a high signal intensity at 1471.04 cm⁻¹ which corresponds to the elongation in the plane of the carboxylic acid (C-O-H) and it is possible to observe an elongation out of the plane at 933.94 cm⁻¹, furthermore, it is also possible to observe the elongation of the carbon-oxygen (C-O) at 1239.13 cm⁻¹.

Other signals which are different from those of the synthesized PCL are present at 2944.24 and 2865.84 cm⁻¹, where it is possible to observe methylene signals that have considerable intensity. These signals result from the large quantity of methylene that originates from fragmentation of the polymeric material. These methods can be useful for degradation of polymers that have similar structure to that of the PCL (see Figure 6), in that case, it could be expected that the process of degradation of such material would be more efficient using a base solution than using an acid solution. This has already been observed in the hydrolysis and degradation of polyesters which have similar structure to that of the PCL [12-14].

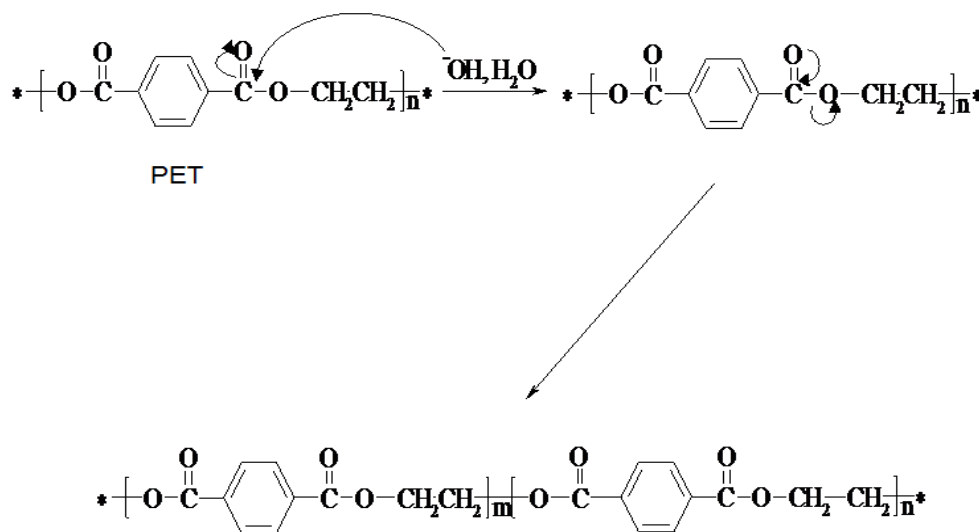


Figure 5. Suggested alkaline degradation mechanism of poly(ethylene terephthalate), where "m" is less than "n" [11]



Figure 6. Residue degradation of PCL

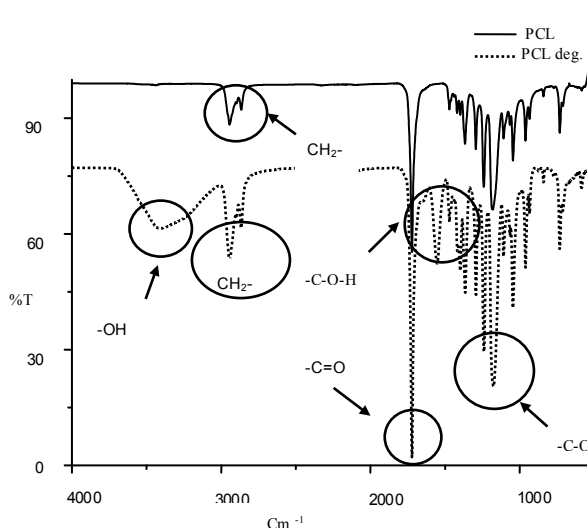


Figure 7. The comparison FT-IR spectra of PCL and PCL non-degraded

4. Conclusions

The comparison reported in this work between the chemical degradation of PCL using acid and base solutions, allows us to conclude that when we used base solutions we obtained better degradation results than when we used acid solutions. This is due to the fact that the degradation process is faster and more efficient in alkaline media. In basic solutions the nucleophilic (OH^-) and electrophilic (K^+ , Na^+) entities react with the monomer of the repeating unit of the polymer more easily than when using acid [Cl^- , $(\text{SO}_4)^{2-}$, H^+], this reaction fractures the polymeric chain of the PCL and as a result the oligomers are obtained. The degradation type that PCL exhibits probably could be present in polymers that have similar structure. With regards to the basic solutions used in this work, the most effective solution for degradation was NaOH.

ACKNOWLEDGMENTS

We are grateful to Jared J. Gerschler, Leticia Medina Saldaña and the University of Papaloapan for the support required to accomplish this research work.

REFERENCES

- [1] Martínez, G., Matos M., Sabino, M., Urbina de Navarro, C., Barrios, C., Taddei, Sajo, A., Arnal, M., Müller, A., Study of a binary mixture biodegradable: polycaprolactone /chitin", *Rev. Iberoamericana de polimeros*, 3(9): 313-321, 2008.
- [2] Martínez G, Urbina de Navarro C, Barrios C, Matos M, Sabino M, Müller A.J, Taddei A, Castelli C. Crystallization, morphology and enzymatic degradation of polyhydroxybutyrate/polycaprolacton, *J. Macromolecular Chemistry and Physics*, 208, 924-937, 2007.
- [3] Chang yong, C., Young Tai-Hyoung, K., Mi-Kyeong, J., Chong Su, C., Jae-Woon, N., Preparation and Characterizations of Poly(ethylene glycol)-Poly(ϵ -caprolactone) Block Copolymer Nanoparticles, *Bull. Korean Chem. Soc.* 2005, 4(26), 523-528, 2005.
- [4] Báez García, E., Ramírez Hernández, A., Marcos A., Synthesis, characterization, and degradation of poly (ethylen *e-b-ε*-caprolactone) diblock copolymer *Polym. Adv. Technol.* 21(1),55-64, 2010.
- [5] Jenkins, M., Harrison, K., The effect of molecular weight on the crystallization kinetics of polycaprolactone, *Polym. Adv. Technol.* 17(6), 474-478, 2006.
- [6] Lian song, W., Zhiping, Z., Hechun, C., Shenglan Z., Chengdong, X., Preparation and characterization of biodegradable thermoplastic Elastomers (PLCA/PLGA

- blends), *J. Polym. Res.* 2010,17(1), 77-82, 2010.
- [7] Shao bing, Z., Z., Xianmo, D., Hua, Y., Biodegradable poly(ϵ -caprolactone) poly(ethylene glycol) block copolymers: characterization and their use as drugcarriers for a controlled delivery system, *Bioamaterials*, 24, 3563-3570, 2003.
- [8] Abe, H., Takahashi, N., Ju Kim, K., Mochizuki, M., Doi Y., Thermal Degradation Processes of End-Capped Poly (l-lactide)s in the Presence and Absence of Residual Zinc Catalyst, *Biomacromolecules*, 5(4), 1480-1488, 2004.
- [9] Báez, J.E., Poli(ϵ -caprolactone), degradable polymer: synthesis triisopropoxide aluminum Al (OiPr)₃ as initiator, *Education chemistry*, 17(4), 458-463, 2006.
- [10] Mukerjee, A., Sinha, V.R, Pruthi, V., Preparation and Characterization of Poly- ϵ -caprolactone Particles for Controlled Insulin delivery, *Journal of biomedical and Pharmaceutical engineering*, 1(1), 40-44, 2007.
- [11] A. Ramírez. 2002. Study depolymerization of poly (ethylene terephthalate). [online]. Available: <http://quimica.ugto.mx...> 2007
- [12] Rahman, M., Alfaro., M., Degradation of polyester geotextiles in alkaline solutions under applied loading. Dep. University of Manitoba, Winnipeg, Canada. Géo Québec. 2004; 33-39.
- [13] Muralidharak, S., Sreenivasan, S., Thermal degradation and burning behavior of cotton polyester and polyester/cotton blended upholstery, *World Applied Sciences Journal*, 9 (11), 1272-1279, 2010.
- [14] Sanz, B. C., Salvador, M. D., Segovia López, F., Borrás, V., Pérez, A.T., Reinforced Plastics chemical degradation in basic media, *VIII National Congress of Mechanical Properties of Solids*. Gandia, 341-347, 2002.