# Characterization of mechanical behavior of biodegradable polymer polycaprolactone after hydrolytic degradation

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**Abstract.** *In tissue engineering, the use of scaffolds for non-vascularized tissue regeneration is a recent application, which presents a more satisfactory result when these are naturally eroded and assimilated during tissue regeneration. In the process of scaffolds design, to select an optimal biodegradable material, one must know the mechanical behavior during degradation. Thus, the present work shows a methodology to characterize the mechanical behavior during degradation of one of these biodegradable polymers, the polycaprolactone (PCL). Their mechanical characteristics are interesting in many soft tissue applications. To characterize the mechanical behavior during degradation, samples were manufactured by Fused Deposition Modelling (FDM) technology, which is closely linked with the personalized scaffolds fabrication and is able to create complex geometries. These samples were degraded at different stages of time in a thermostatic bath at 37º and pH 7,4. Finally, samples were tensile tested. The results showed an increase of stiffness and tensile strength.*

*Key words: Biodegradable polymers. Hydrolytic degradation. Polycaprolactone. Mechanical characterization.*

## 1. INTRODUÇÃO

Nowadays, there is huge variety of biodegradable materials that can be found commercially and in different applications on tissue engineering. These materials have distinct mechanical behaviors and degradation rates and they can be selected according the application requirements. With the advent of regenerative medicine, biodegradable materials gained an important function. They are molded in complex structures that temporarily replace the mechanical functions of biologic tissues, then they degrade during tissue regeneration and are finally eroded and assimilated by the host body. In the presence of water molecules, the chemical bonds of the biodegradable polymers are prone to undergo hydrolysis. This phenomenon causes irreversible changes in the mechanical behavior of biodegradable polymers. When a biodegradable polymeric device is immersed in water, water initially diffuses into the material. The presence of water triggers chemical degradation of the polymer, resulting in cleavage of the molecules. During this degradation, there is the loss of mechanical properties and material performance, i.e., there is loss of mechanical strength, toughness and stiffness. In the case of aliphatic polymers, such as PCL and polylactic acid, each polymer macromolecule is an immense chain of functional groups, with a carboxylic radical and alcohol group at each end. In the presence of water, the molecules are randomly divided into two, in a given ester group. Figure 1 illustrates the most common scheme of the degradation mechanism via hydrolysis. Thus, the number of ends, and consequently the number of carboxyl groups, will increase with the degradation time, while the molecules are divided during the hydrolysis process.

Therefore, it is important to characterize the material properties during hydrolytic degradation. The degradation media must be carefully selected to simulate the degradation environment present in human body, since the degradation is affected by temperature, stress field and pH of degradation environment (Vieira *et al.*, 2014). Besides the hydrolytic degradation issue, the mechanical behavior of PCL is a complex viscoplastic behavior. On one hand its relaxed configuration in monotonic quasi-static test is non-linear. On the other hand it is strongly temperature and time dependent. Hence, it is also important to take in account the strain rate used during mechanical tensile tests. This must be in accordance with the application. Furthermore, when a constant stress is applied they exhibit creep, or they show stress relaxation when submitted to a constant deformation.
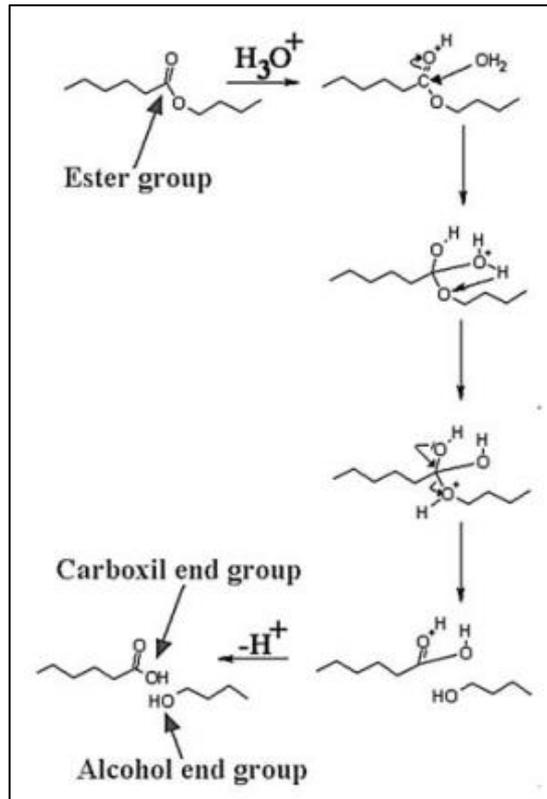
Figure 1: Scheme of the acid based hydrolysis mechanism, Vieira *et al.* (2011).

## 2. METHODS

Samples were manufactured from the biodegradable polymer polycaprolactone using additive manufacturing by FDM technology, according to ASTM D638 (type IV) dimensions, see Fig. (2). The samples thickness needs to be as minimal as possible to promote homogeneous erosion, and to consider the hypothesis of instantaneous diffusion of water. Therefore, samples were manufactured with an average thickness of approximately 1 mm. Then samples were placed in a thermostatic bath at 37ºC and pH 7,4, to simulate *in vitro* the human body equilibrium conditions *in vivo*. During degradation, no load was applied to samples. Six samples for each degradation stage were used. Different degradation stages of 0, 2, 4, 8, 16 and 32 weeks were used. Before tensile tests, samples were dried in stove at 37º for one week to stop degradation. Finally, samples were monotonic tensile tested at displacement rates of 1 mm/min. and 200 mm/min. Due to the high level of deformation of the PCL, the tests were completed at the beginning of necking. Three samples were used for each displacement rate.
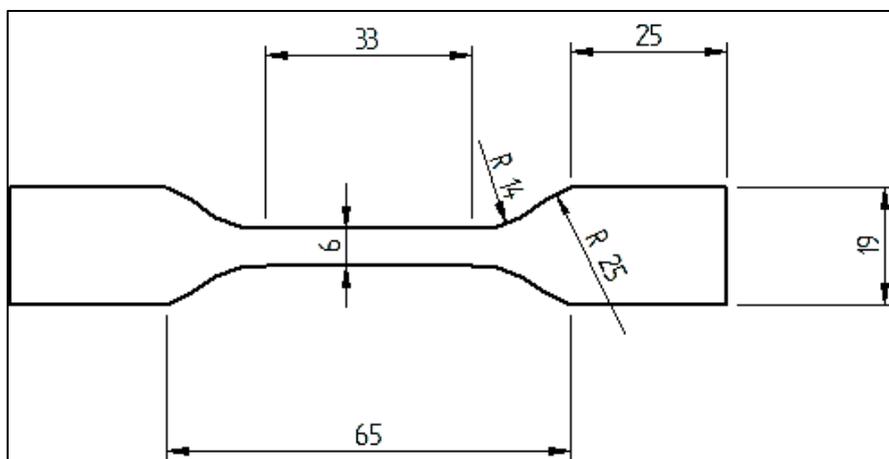


Figure 2: Geometry and dimensions (in millimeters) according to ASTM D638-02a.

## 3. RESULTS AND DISCUSSION

Mean and standard deviation for the tensile tests results are presented in the Fig. (3) for the different displacement rates and degradation times. Furthermore, as expected, it is possible to observe that for higher strain rates the material presents a higher tensile strength and stiffness. In Table 1, it is possible analyze the increase of mechanical properties for the same displacement rate. The mechanical behavior and properties of semicrystalline polymers are directly related to their degree of crystallinity and molecular weight. Increasing the degree of crystallinity results in a higher stiffness and mechanical strength of the polymer as well as increased molecular weight. For semicrystalline polymers, such as PCL, the hydrolysis process will preferably initiate in the amorphous regions. Thus, an increase in PCL properties is expected during the initial stages of degradation, since with the initial degradation of the amorphous phase the percentage of crystalline phase will be larger in relation to the volume of the material. Therefore, the results were directly influenced by the increase of crystalline phase percentage, since this phase has higher stiffness and mechanical strength. Similar results were obtained by Lam *et al.* (2008).
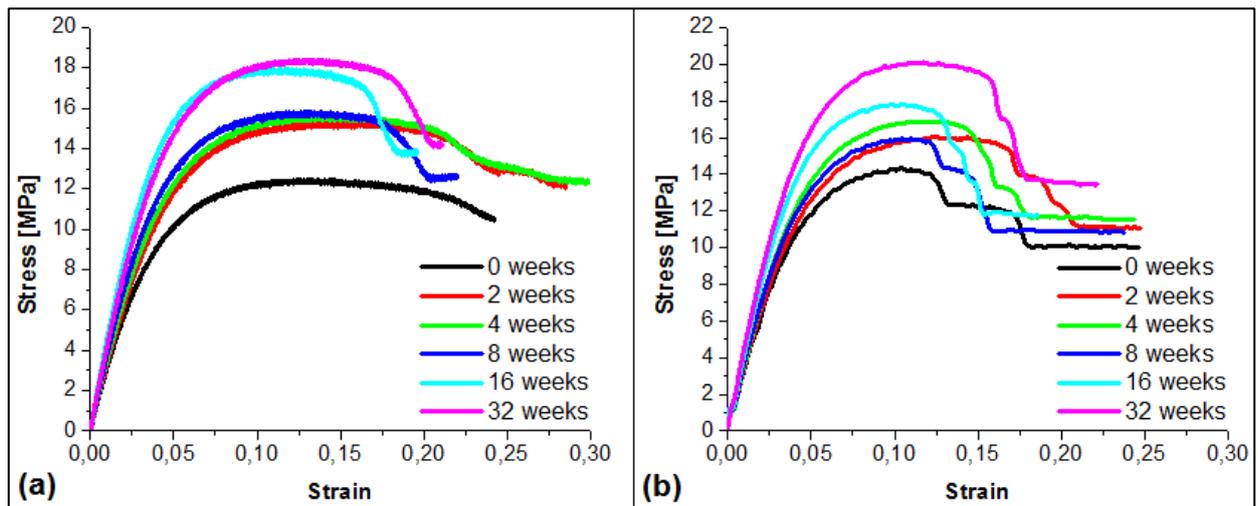


Figure 2: Engineering stress-strain curves for PCL with different degradation stages and displacement rates: (a) 1 mm/min. and (b) 200 mm/min.

Table 1 – Mechanicals properties of PCL: $S_m$: tensile strength; ε: strain at tensile strength; $E$: Young modulus.

| | 0 semanas | 2 semanas | 4 semanas | 8 semanas | 16 semanas | 32 semanas |
|---|---|---|---|---|---|---|
| | | | 1mm/min. | | | |
| $S_m$ [MPa] | 12,59±0,55 | 15,48±0,32 | 15,7±0,51 | 15,94±0,35 | 17,93±0,41 | 18,43±0,44 |
| ε | 0,13±0,03 | 0,15±0,02 | 0.15±0,02 | 0,13±0,001 | 0,11±0,002 | 0,12±0,002 |
| $E$ [MPa] | 309,9±4,9 | 330,7±1,2 | 354,4±9,9 | 376,1±2.96 | 417,24±1,65 | 384,89±12,49 |
| | | | 200mm/min. | | | |
| $S_m$ [MPa] | 14,4±0,43 | 16,07±0,86 | 16,92±0,61 | 16,01±0,36 | 17,78±0,55 | 20,14±0,61 |
| ε | 0,12±0,001 | 0,13±0,001 | 0,12±0,01 | 0,12±0,01 | 0,09±0,004 | 0,11±0,003 |
| $E$ [MPa] | 336,29±7,9 | 354±9,5 | 391,9±18,5 | 413,13±7 | 407,4±11,26 | 423,63±6,69 |

## 5. CONCLUSIONS

In this work, degradation tests of PCL specimens with different stages of degradation (0, 2, 4, 8, 16 and 32 weeks) were performed and the results showed an initial increase in stiffness and tensile strength, a behavior compatible with that found in literature. Since hydrolytic degradation is characterized by weakening of the mechanical properties, the results obtained showed the need for a longer degradation time for hydrolytic damage to PCL, since the 32-week period was only sufficient to hypothetically degrade the amorphous regions of the polymer. Therefore, the low degradation rate of PCL makes it compatible for long-term scaffold design.

## 6. REFERENCES

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## 7. ACKNOWLEDGMENTS

## 8. RESPONSIBILITY FOR INFORMATION

The authors are solely responsible for the information included in this work.