The double torsion test for evaluation of fracture toughness of PLLA bioresorbable polymer during degradation

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Abstract

Poly-l-lactic acid (PLLA) is widely used in the fabrication of bioresorbable orthopaedic and bone fixation devices. These implants degrade over time within the in vivo environment increasing the risk of potential mechanical failure. Therefore it is necessary to better understand the fracture behaviour of PLLA under physiological conditions during the degradation process. The aim of this work was to estimate how its fracture properties would change once a PLLA device has been implanted in a patient's body and commenced degradation. PLLA specimens were compression moulded and degraded at 70 ℃ in PBS (the elevated temperature ensured accelerated degradation). As PLLA had rarely been studied using the double torsion (DT) test, some preliminary validation tests were also conducted in order to optimise the specimen geometry to achieve consistent behaviour. Tests were conducted after 1, 3 and 7 days of accelerated in vitro degradation. It was possible to determine the fracture toughness from the DT technique for up to 3 days of degradation.

Fracture toughness deteriorated dramatically between 1 and 3 days of degradation from 4.45 ± 0.42 to 2.06 ± 0.20 MPam$^{1/2}$. Beyond 3 days the extent of degradation prevented testing by the DT technique.

Keywords: double torsion test; bioresorbable polymer; poly-l-lactide, degradation, medical implants

1. Introduction

Homogenous poly-L-lactidic acid (PLLA) is widely used in the repair of severely injured bone in the form of pins, plates, screws and other implantable devices. However, it has been reported in the literature that it sometimes fractures or breaks into fragments. Thus, it is necessary to better understand the changes in PLLA's fracture behaviour as it degrades after implantation in a patient's body in order to design safe implant devices when it comes to fracture related failure [[1]-[3]].

Knowledge about material strength, toughness, deformation and fracture mechanisms, as well as the interplay between those material properties, are basic pre requisites for estimating a product's reliability and optimising it. One means of obtaining this is through developing reproducible test methods which are capable of accessing geometry independent parameters, i.e. material properties. Some basic knowledge from the testing and evaluation of metallic materials might be used as a starting point, but particularities of polymeric materials such as the influence of temperature and strain rate in their behaviour must be taken into account [[4]]. In this context, the Double Torsion (DT) test has been successfully applied along with a Fracture Mechanics approach in the study of mode I polymer fracture [5]. Its main advantage is that it is not necessary to measure the crack size a to calculate K_{IC}, which is convenient when testing opaque materials or in controlled environments and avoids a source of error. Furthermore, the technique is easier to use for studying slow crack growth than compact tension or single edge notch bend [[6]]. For PLLA no examples of it being applied in the literature can be found. Therefore applying the DT test to PLLA requires some preliminary tests to optimise the test method in order to achieve predictable specimen behaviour and validate it.

Semi-crystalline PLLA macrostructure consists of a crystalline and an amorphous phase [[7]]. When submitted to degradation in an aqueous environment, it undergoes heterogeneous bulk erosion via chain scission, with water first diffusing in the polymer's amorphous regions, which allow easier water penetration than the densely packed crystalline regions [[8]] and thus are preferentially degraded. Amorphous PLLA crystallizes as it degrades and therefore it grows resistant to hydrolytic attack, consequently the degradation process can take up to five years in physiological conditions. Such longevity poses a difficulty in performing degradation tests and hence motivated the development of accelerated degradation techniques. It has been reported that the degradation mechanism of semi-crystalline PLLA was not greatly affected above its glass transition temperature because its molecules were tightly packed within the crystalline domains. Hence, it is possible to correlate the results of such accelerated tests to the actual material behaviour in physiological conditions [[9], [10]]. Accelerated test techniques were used in this study due to the time constraints of testing at rates correlating to in vivo degradation.

The aim of this study was to optimise the DT test procedure for the bioresorbable polymer PLLA and obtain values for fracture toughness at various stages of hydrolytic degradation.

2. Materials and Methods

PURASORB® PL38 (Corbion Purac Biomaterials, The Netherlands), supplied in pellet form, was compression moulded into flat specimens of 1.6 mm thickness using a heated platen press. The mould and pre-weighed PLLA was placed on the preheated platen press (200 ℃) for 5 minutes, so that the temperature would stabilise through the mould and polymer. Then a compressive pressure was applied to it for 1 minute. Next, the mould was immediately released from the press and allowed to cool for 20 ± 1 minutes. After that the specimens were annealed in a convection oven (Genlab Ltd., Widnes, Cheshire, UK) at 120 ℃ for approximately 4 hours. The annealed specimens were dry cut by CNC machining (Figure 1) with one set of specimens including a central groove and one set excluding this feature. The specimens with no CNC machined groove had a line manually scribed along their centreline with a sharp craft knife blade. To avoid degradation by atmospheric moisture, specimens were dried in a vacuum oven following machining (Sheldon Manufacturing Inc., USA) for three days at 40 ± 1 ℃ in a 74 ± 2 cm Hg vacuum and then stored in a desiccator cabinet. Finally,

specimens were labelled, weighted using an analytical balance and dimensions measured with a digital calliper.

Specimens were placed in sterilize plastic bottles containing 150 ml of phosphate buffer solution (PBS) (pH 7.4 $\pm$ 0.05) and degraded at 70 $\pm$ 1 ℃ in a convection oven then removed after 1, 3 and 7 Days and cooled to room temperature. The degraded specimens were tested at room temperature fully immersed in PBS.

Since the objective was evaluation of mechanical properties of PLLA in physiological conditions control specimens were also immersed in PBS at room temperature for 3 days, to make sure they were hydrated to simulate physiological conditions.

During testing specimens were supported along their length by two 3 mm rollers on each side, with their centres 30 mm apart. A single screw mechanical testing machine (LLOYD Instruments LTD, UK) was used. The load was applied at a constant rate of 1 mm/min by two 6 mm ball bearings, which had their centres 10 mm apart and were symmetrically positioned at each side of the notch (Figure 2). Thus, the specimen was subjected to double torsion bending. The specimens were carefully aligned to the test jig to ensure they would be subjected to mode I fracture only. A test was considered successful if cracking initiated at the notch and propagated along the centreline of the specimen.

The crack initiation (onset of cracking) was identified on the PLLA load versus displacement curves as the point on the curve where a significant change in the stiffness [[2]] ($dP/d\delta$) of the specimen was first observed (Figure 3). The experimental points were imported into the software MatLab® R2012a, then the portions of the load vs displacement curve identified as representing elastic deformation and onset of cracking were interpolated by a 10th degree polynomial. That polynomial was differentiated in respect to the displacement to obtain $dP/d\delta$. Also, the energy to fracture was calculated by numerical integration of the load vs displacement curve from its beginning to the onset of cracking. The fracture toughness K_{IC} was calculated using a linear elastic fracture mechanics approach [11-12]. For this the load at onset of cracking (P_c) was substituted into equation 1, where W_m is the moment arm, υ is the Poisson's ratio, t is the specimen thickness, t_n is the specimen thickness at the crack plane and W is the distance between supports.

$$K_{IC} = P_c W_m \left[\frac{3(1+\upsilon)}{W t_n t^3} \right]^{\frac{1}{2}}$$

Equation 1

After testing, the specimens' surfaces were dried with a paper towel and the specimens were reweighted. Their hydration rate was calculated using equation 2.

$$\text{Hydration rate (\%)}=100\times\frac{\text{Weight}_{\text{after testing}}-\text{Weight}_{\text{before immersion}}}{\text{Weight}_{\text{before immersion}}}$$

Equation 2

3. Results and Discussion

During degradation testing the hydration rates were observed to increase in a seemingly non-linear manner with the most significant increase in hydration occurring after the first day of degradation ($0.59\pm0.01\%$). On the third and seventh days, the average hydration rates were $0.70\pm0.1\%$ and $0.83\pm0.07\%$, respectively. These results concur with those of Weir et al [10] where it was shown that wet mass started to plateau after one day degradation at 70 ℃ and did not show a downward trend until beyond 15 days, at which point physical mass loss of the polymer into the surrounding medium was proposed to occur.

The DT tests of the manually scribed specimens were inconclusive when it came to accessing PLLA fracture toughness in any stage of degradation. Cracking would tend to initiate under the ball bearings rather than in the middle of the notch, and cracks were frequently asymmetrical relative to the specimen centreline.

For DT testing of the grooved specimens, crazing during fracture was observable through the appearance of white regions and lines close to the crack tip during the test. Particularly for specimens degraded for 3 days, it was observed that crack propagation occurred in the following manner: first, crazes would develop and extend from the notch tip, then these crazes would initiate cracks primarily along the groove, with other cracks sometimes branching out from the groove. Some secondary cracking was also observed to occur, directly below the spherical bearings which applied the load; cracks would spread radially from the contact point and eventually joint the crack that ran along the groove (Figure 4). Thus cracking occurred in two stages, each one causing an observable change in the slope of the Load vs. Displacement curve (Figure 5). The onset of cracking (P_c) was taken from the first significant change in slope. The second change in inclination was invariably much more accentuated than the first. By the second stage, a significant amount of crazing could be observed at the crack tip and the LEFM approach was no longer be considered valid due to the large deformations.

After 7 Days of degradation the samples were very fragile and handling could easily damage them. An increasing trend in the appearance of whitened regions on the body of the samples with the number of days of degradation was apparent. It was also noticed while testing these samples that that the whitened regions would initiate and/or deflect cracks as the load increased (Figure 6).

K_{IC} and energy to fracture were calculated for the PLLA soaked in PBS at room temperature and after 1 and 3 days of accelerated degradation (Figure 7 and 8). It was not possible to calculate K_{IC} after 7 days of degradation because the cracks did not reliably travel along the grooves.

Although no crystallinity measurements were made in this study, the previous results of Weir et al [13] and Park et al [14] suggest that the specimen's initial crystallinity would be between 40% and 50% as determined by differential scanning calorimetry.

The increase in the appearance of white regions on the body of the samples with the number of days of degradation was attributed to heterogeneous degradation within the samples and has previously been reported [10]. It is believed these regions interfere significantly in the stress field within the specimens during mechanical testing by concentrating stresses. They initiated cracks and the fact that cracks would rather develop through these white regions after 7 days of degradation also suggest lower toughness, compared to the surrounding material.

Although literature [6,15] recommends using a groove as small as possible, or even no grooving at all, the results showed that for PLLA a manually scribbled groove was not sufficient to guide the crack path. It was hypothesised that the groove concentrated less stress than the specimen's inhomogeneities and defects; so cracking occurred preferably around the latter regions rather than along the groove. That also gives rise to the observation that PLLA cracking might be remarkably sensitive to the conditions around crack tip.

The results obtained for the grooved specimens were compared to the ones obtained by Park et al [16] for semi-crystalline PLA, compression moulded and annealed, tested in air using the SENB technique at cross-head speed of 1 mm/min. Those authors obtained the value of 3.6 ± 0.2 MPa.m$^{1/2}$ for K_{IC}. The K_{IC} value obtained by Park et al [16] is lower than the values obtained for non-degraded PLLA and the PLLA degraded for Day 1. It can be argued that at the beginning of the degradation process the fracture toughness of the material in the current study might be enhanced by the plasticizing effect of water. A significant drop in K_{IC} was detected at Day 3 of degradation. At this point, the crystallization of the material and its

consequent embrittlement, as well as the chain scission of its molecules, may have outweighed the plasticizing effect of water and, consequently, the material exhibited brittle behaviour. That embrittlement is also reflected by the drop in the energy to fracture, as cracking would start at lower loads and shorter displacements as the degradation process advanced. This agrees with the idea that PLLA would become fragile and lose mechanical strength as it degrades, as previously observed [10].

To calculate degradation times at 70 ℃ that would be equivalent to the degradation times under physiological conditions, i.e. 37 ℃, molecular weight data and a correlation described by Weir et al [10] for PLLA degraded at those conditions were used. That correlation was derived based on molecular weight decrease during degradation (Equation 3). Since the same authors found that PLLA's mechanical properties are dependent on molecular weight, regardless of rate of degradation, using the aforementioned correlation was considered adequate.

$$\boldsymbol{ln\left(\frac{M_{nt}}{M_0}\right) = -kt}$$

Equation 3

The data on molecular weight and the model obtained by Weir et al [10] permit estimating the equivalency between degradation times at 37 ℃ and 70 ℃ (Table 2) and thus correlating the drop in fracture toughness observed above with what might be observed in physiological conditions.

4. Conclusion

The fracture behaviour of PLLA has been studied in different stages of degradation and findings suggest that a deep central groove is necessary to guide the crack propagation especially at later stages in degradation as the material develops inherent brittleness. In the absence of said feature, cracking behaviour is predominantly determined by the non-homogeneous material structure and degradation pattern, which generally leads to asymmetrical crack propagation and inconclusive test results. Determination of crack initiation from the load vs displacement curve was most precise through interpretation of the curve's first derivative. It was possible to measure the fracture toughness of PLLA for up to 3 days of accelerated degradation. Furthermore it was estimated that 3 days of accelerated degradation was equivalent to 6 months of degradation under physiological conditions.

PLLA is commonly used in facture fixation devices, such as screws and bone plates. Fracture toughness is considered an important property in such devices as it will dictate the material's tendency to fracture and fragment during the later stages of degradation, but prior to significant mass loss (bioresorption). This work represents an in initial step in developing a valid test for monitoring and predicting fracture toughness of bioresorbable polymers during their degradation process.

Figures and Tables

Table 1: Molecular Weight vs Time and Model Constant k at 37 ℃ and 70 ℃. Adapted from Weir et al [10]

								k
Days at 37 ℃	**0**	**28**	**70**	**140**	**182**	**224**	**226**	0.0052
Mol. Wt. at 37 ℃	158,000	143,000	120,000	72,5000	93,850	65,800	53,050	
Days at 70 ℃	**0**	**1**	**3**	**5**	**9**	**14**	**18**	0.2155
Mol. Wt. at 70 ℃	166,000	119,000	64,450	39,300	24,900	29,200	13,750	

Table 2: Equivalent Degradation Times in Physiological Conditions for the Experimental Degradation Times.

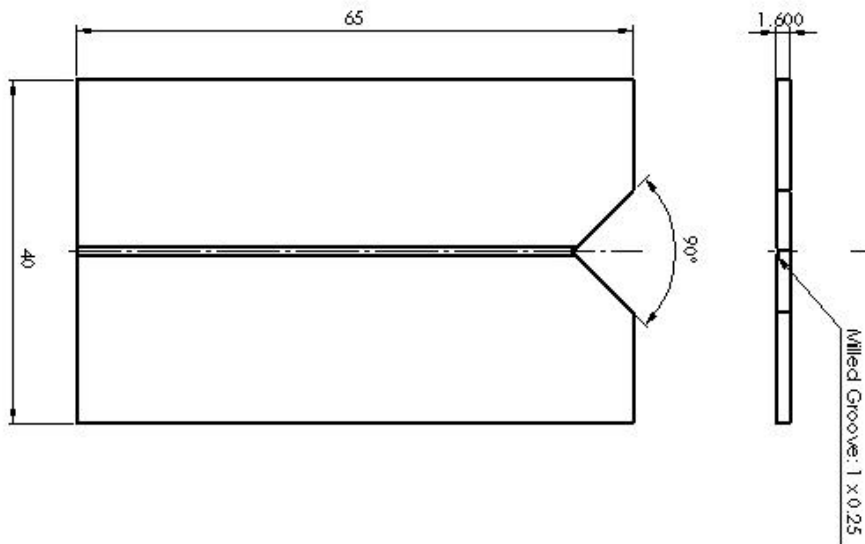| Experimental Degradation Times (accelerated conditions)	Predicted Degradation Times in Physiological Conditions	Experimentally determined Fracture Toughness, K_{IC}, MN.m$^{1/2}$
Soaked at Room Temperature	1-2 Days at 37 ℃	5.94 ±0.97
1 Day at 70 ℃	64 Days at 37 ℃	4.45 ±0.42
3 Days at 70 ℃	181 Days at 37 ℃	2.06 ±0.20
7 Days at 70 ℃	290 Days at 37 ℃	Not available

Figure 1: DT test specimen geometry. Nominal dimensions are in millimetres.
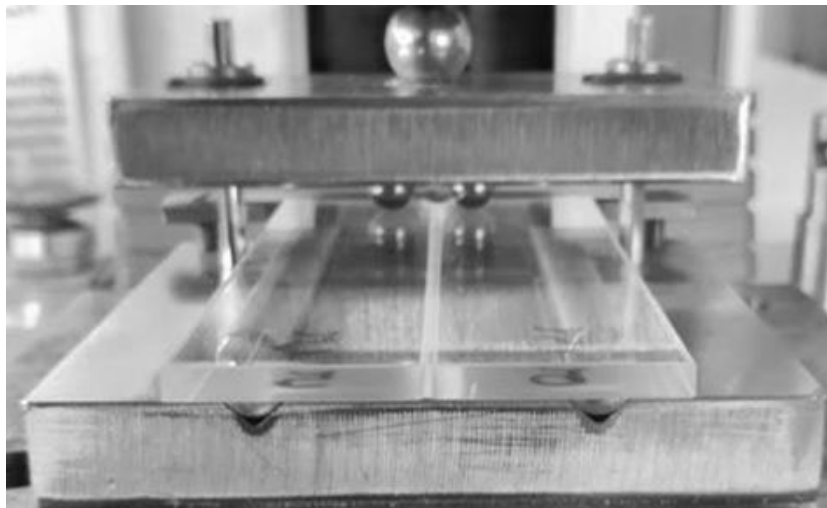

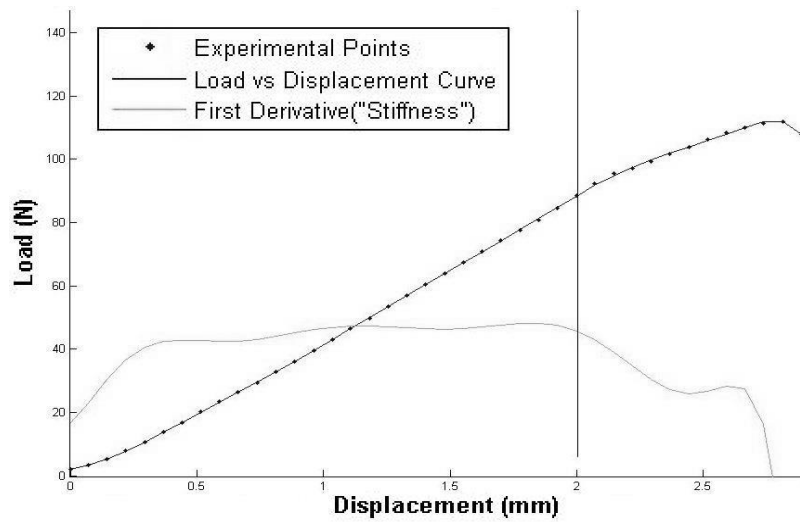**Figure 2. Assembled test jig with a 3mm Perspex® specimen positioned in it (groove on lower face).**

Figure 3: First portion of Load vs Displacement curve for a PLLA sample degraded 1 day in PBS at 70 ℃ - the vertical line marks the onset of cracking.
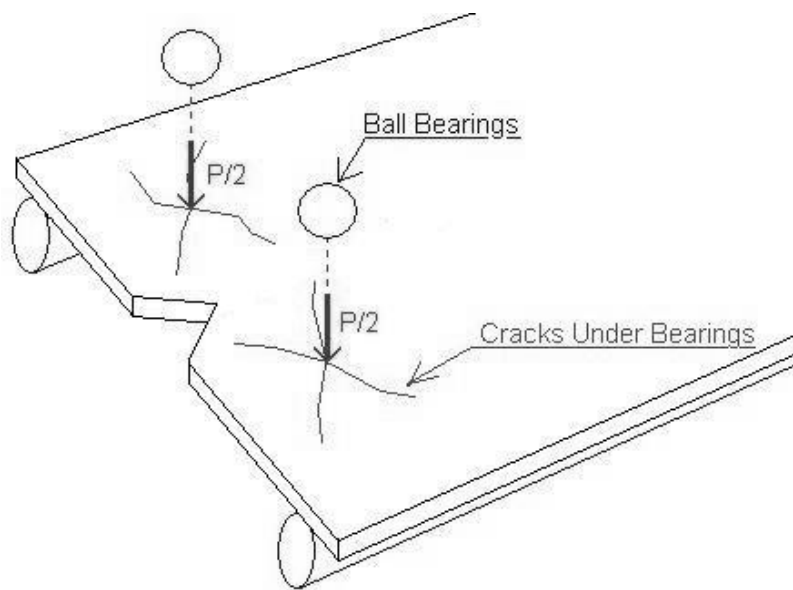

Figure 4: Schematic of contact between ball bearings and specimen showing the secondary cracks that developed under the bearings.
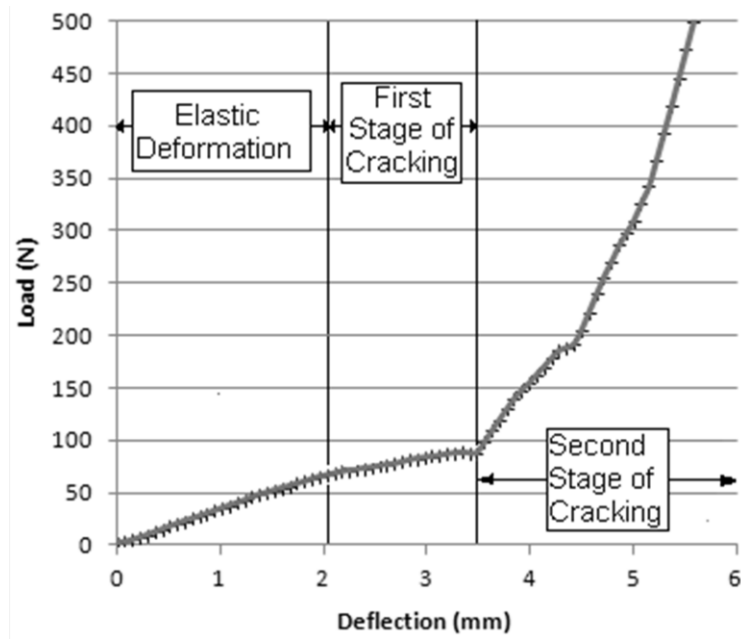
Figure 5: Stages of Cracking as They Appear in a Load vs Displacement Curve of a PLLA Specimen Degraded up to 3 Days in PBS at 70 ℃ and Tested at 37.5±1 ℃.
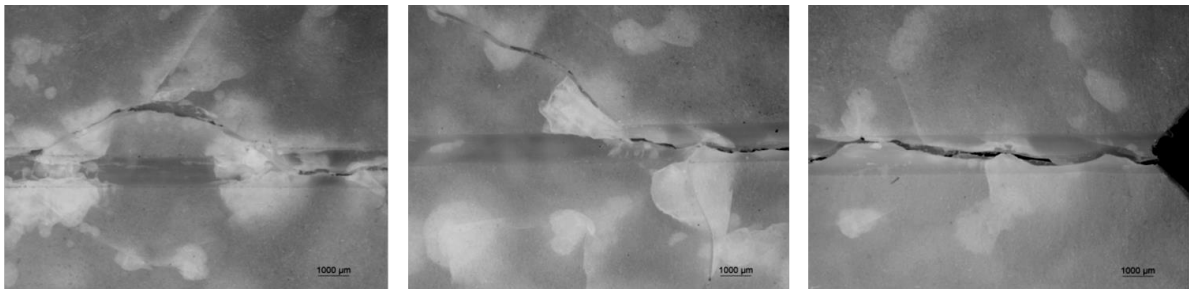

Figure 6: : Grooved PLLA Samples (1i and 4i) after 7 Days of Degradation in PBS at 70 °C and the DT Test. Note the preferential crack propagation through the white regions.
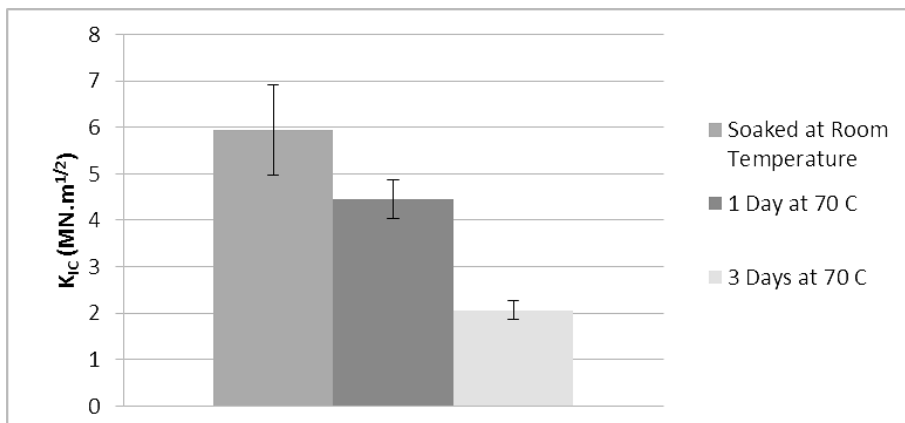

Figure 7: K_{IC} of PLLA after Different Degradation Times
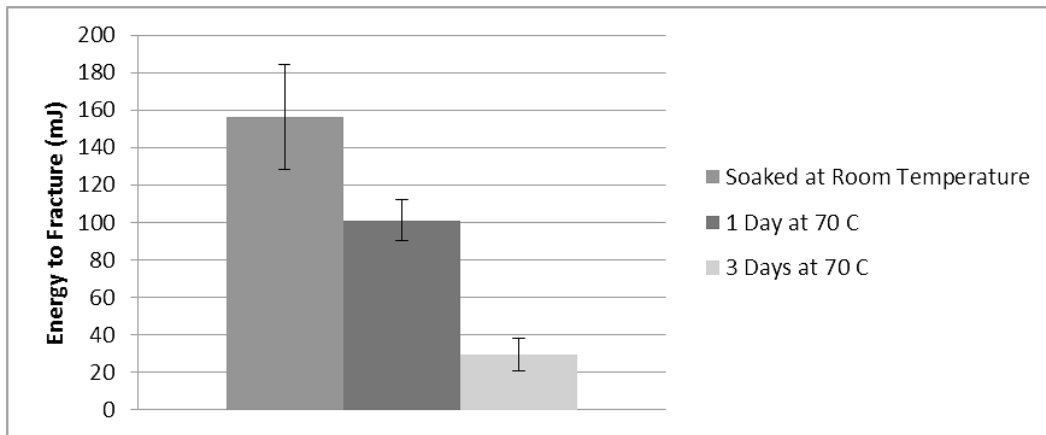
Figure 8: Energy to Fracture of PLLA after Different Degradation Times

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