Degradation of Polymeric Material used for Osteosynthesis and Comparison of Fracture Toughness Between Test and FEA

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ABSTRACT

Biodegradable polymers such as PLA, PGA, PLGA etc., inside the human body often pose a tough challenge for the orthopedic doctors and material scientists. Unlike metallic or ceramic implants, where deterioration of the mechanical properties has never been an issue, biodegradable polymeric implants, used for Osteosynthesis, deteriorate while the fractured bone is subjected to kinesiological stress during healing process. To understand how biodegradable materials lose its mechanical properties, an investigation into the influence of degradation process on Mode-I fracture toughness of poly (lactide-co-glycolide), PLGA 85:15 material was initiated. The objective of this study was to build an improved understanding of the deterioration of biodegradable polymers mechanical properties during in-vitro degradation and how this change may affect long term in-vivo performance of the implants. A simple mathematical relationship was established to understand the change in the Young’s modulus during the degradation process. Compact tension specimens were designed and molded for mode-I fracture criterion and then put in 3% concentrated Hydrogen peroxide (H2O2) to study the degradation process. FEA (Finite Element Analysis) was used to study the change in mechanical properties and then the results were compared with the physical test. Mode-I fracture toughness, K\text{IC} was measured and the behavior of the polymer was also identified. It was seen that the fracture toughness, K\text{IC} of PLGA 85:15 decreased with the progression of degradation. Finally, it was concluded that an increase in the Young’s modulus made PLGA 85:15 very brittle and hence resulted in reduced fracture toughness.

Key words: Biodegradable polymeric implants; PLGA 85:15; Osteosynthesis; in-vitro degradation; Hydrogen peroxide; Mode-I fracture; Young’s modulus; FEA; xFEM (Extended Finite Element Method); Fracture toughness; K\text{IC}

INTRODUCTION

Biodegradable polymers have been the topic of many research studies\cite{1,2,3}. Significant advancements have been made in the development of biodegradable materials and their applications in the past decade or two\cite{4}. Many implantable devices are made from polymeric materials\cite{5,6}. These polymeric materials ensure a wide range of functionality such as structural support, electrical insulation, bio friendly and biocompatibility inside the human body. In such roles, stability and integrity of the polymer over the period of its intended use is of utmost importance. Poly (lactide-co-glycolide),
PLGA is a copolymer of lactic acid and glycolic acid\textsuperscript{[10]}. PLGA has been used in many fixation devices for bone fracture\textsuperscript{[11-13]}. There are many advantages of using biodegradable fixation devices as opposed to using metallic or ceramic implants\textsuperscript{[14]}.

One advantage is the postoperative assessment\textsuperscript{[15,16]}. Since biodegradable implants are generally transparent or semitransparent, radiographic imaging, such as X-ray, MRI, CT scan etc. of the healing bone is easier for progressive assessment and evaluation\textsuperscript{[17]}. Furthermore, no after surgery is required to extract the implant since it dissolves during physiological processes and is excreted in normal metabolic processes. Also, they are not as rigid as titanium, ceramic or steel which cause stress shielding and do not produce clinical reactions such as, allergies or toxicity that can occur with metallic implants\textsuperscript{[18,19]}.

There are of course disadvantages associated with biodegradable implants; the most critical one being possible premature failure under different loading conditions inside the human body, giving rise to crack initiation and propagation leading to failure of the implant\textsuperscript{[22-24]}. Despite such fear of failure of implants, the usage of biodegradable polymers has gone up. Therefore, in-vitro studies and testing are being done in laboratories around the world to understand the effect of degradation of biodegradable polymers inside the human body\textsuperscript{[25,26]}.

As per the surveyed literature, most of these research studies are heavily focused on changes in the physical and chemical properties of such biodegradable polymers\textsuperscript{[25,26]}. The change in mechanical properties, during degradation, are often ignored. To better understand how these biodegradable polymers lose their mechanical strength, a thorough study was conducted to investigate the influence of the degradation\textsuperscript{[27]}.

Linear Elastic Fracture Mechanics (LEFM) is a widely used technique to study fracture mechanics of brittle material\textsuperscript{[28]}. FEA models based on Extended Finite Element Model (XFEM)\textsuperscript{[28]} were built and simulation was run at each stage of the degradation.

Fracture toughness is an important mechanical property of a material. It is a measurement of resistance to the crack growth when a critical stress is reached. In simple terms, it is defined as a quantitative way of expressing resistance to brittle fracture in the presence of a crack\textsuperscript{[29,30]}. All the mechanical failures are put in three categories, namely Mode-I, Mode-II, and Mode-III fracture or the combination of two or three modes. Mode-I is also known as opening mode. It occurs when loading and therefore, the stresses are perpendicular to the plane of fracture. Mode-II is also called sliding mode and occurs when the shear stresses are in the plane of fracture. Mode-III is also known as tearing mode and occurs when shear stresses are out of plane of fracture. Since Mode-I fracture is commonly occurring and considered as the most dangerous mode of fracture it was considered for this study. Fracture toughness plays an important role in the design of a mechanical part. In this study, fracture toughness was calculated as the biodegradable polymer undergoes \textit{in-vitro} degradation. Fracture toughness testing was done in accordance to the American Society for Testing and Materials (ASTM) for Mode-I fracture and the inferred properties are standardized and accepted as accurate properties\textsuperscript{[31,32]}.

**MATERIAL AND METHOD**

1. Preparation of PLGA 85:15 samples and degradation process

PLGA 85:15 was used in this study. A steel mold was design and machined as shown in Figure 1A and Figure 1B.

A compression molding press was used to manufacture the samples. The density (\(\rho\)) and glass transition temperature (\(T\)) of PLGA 85:15 are given as \(\rho = 0.00134\) gram/mm\(^3\) and \(T=50^\circ\text{C} - 55^\circ\text{C}\).
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The dimension of the sample was 22.5 mm \( \times \) 21.8 mm \( \times \) 9 mm. Therefore, the mass of each sample was calculated as: \[ m = 0.00134 \times 4374 = 5.9 \text{ grams} \].

The PLGA 85:15 pellets were heated 10 \( ^\circ \text{C} \) more than their glass transition temperature at 65 \( ^\circ \text{C} \). The temperature was held constant for one hour. Initially, cyclic pressure was applied to vent out air from the mold cavities. Then, a pressure of 379 MPa was applied gradually to create a set of compact tension specimens. No enforced cooling was applied. The mold was naturally cooled for 8 hours to the room temperature. The samples were once again measured to verify the mass. They were all found to be approximately 5.9 grams. Notches were cut in each specimen and loading holes were drilled as per the ASTM standard D5045 prior to the degradation process as shown in Figure 2A and Figure 2B.

Two samples were tested for fracture as per ASTM standard D5045 before the degradation process was initiated and the force-displacement data was recorded directly from the Universal Testing Machine (UTM). A biomedical implant, made from PLGA 85:15 takes approximately 6 months to 18 months to completely degrade inside the human body. This huge variation depends largely on physiological condition of the recipient. To accelerate the in-vitro degradation process hydrogen peroxide (H\(_2\)O\(_2\)) was chosen. This is because hydrogen peroxide is bio stable, easily available and is also used as degradation medium in other surveyed literatures. The pH factor of a healthy human serum albumin is about 7.4. A 3% concentrated H\(_2\)O\(_2\) is not only bio stable it also has pH factor close to 7.0. A 300 ml of 3% concentration solution of H\(_2\)O\(_2\) was formulated and stored in 8 beakers. Two beakers each were labeled as Day-1, Day-2, Day-3 and Day-4. A total of 8 marked samples were separately immersed in each beaker. The beakers were then placed in an incubator. The incubator is attached to a shaker which continuously shook the incubator at 5 Hz frequency to mimic the physiological processes inside the human body. The temperature inside the incubator was set to 37 \( ^\circ \text{C} \). Every day, for four consecutive days, two samples were taken out and wiped clean. A desiccator was used for 5 hours to remove remaining moisture (H\(_2\)O\(_2\) solution) from the samples.

This study was conducted in a mechanical test lab. It was mainly done with material and machines. No living organism or animal was ever used or harmed in this study.

![Figure 3](image1)

**Figure 3** SEM images of the specimens as degradation progressed.

![Figure 4](image2)

**Figure 4** Specimen mounted between the jaws of Universal Testing Machine.

![Figure 5](image3)

**Figure 5** Sample under tension and opening load.
2. Images from Scanning Electron Microscope (SEM)

A specimen from each day of degradation was studied under the Scanning Electron Microscope (SEM) to see the topographical change on the surface of the specimen. It was observed that as soon as the specimens were dipped in H\textsubscript{2}O\textsubscript{2} solution, degradation started. Initially, the outer surface showed signs of degradation in terms of tiny pockmarks. As the degradation progressed from day-1 to day-4, those tiny pockmarks transformed into micron level holes as shown in Figure 3. Initially, the holes were sparsely distributed on the surface of the specimen. It then progressed towards the core of the specimen. The holes became denser and eventually, the specimen became very porous.

3. Fracture test

A special clevis was designed to hold the specimen and then fitted between the jaws of the Universal Testing Machine (UTS) in accordance with the ASTM standard D5045. The complete assembly is shown in Figure 4. The upper jaw was given a constant velocity of 0.167 mm/sec. The setup was run until the specimen fractured. The force versus displacement curves were recorded directly from the UTS machine.

4. Relationship between Young’s modulus (E) and slope of force-displacement curve (S)

The compact tension specimens made from PLGA 85:15 were tested for mode-I fracture. Under mode-I fracture mode, when load is applied, the sample undergoes a combination of opening load as well as pull load as shown in Figure 5. The front of the specimen is treated as two cantilever beams in bending and the rear of the specimen is treated like a beam under tension.

The slope (E) of the Stress-strain curve and slope (S) of Force-displacement curves are shown in figure 6A and figure 6B.

The total displacement of the sample, under mode-I fracture mode is given as

$$\delta = 2\delta_{\text{load}} + \delta_{\text{axial}}$$  \hspace{1cm} Eq.1

Where

- $\delta_{\text{load}}$: deflection of the cantilever beam
- $\delta_{\text{axial}}$: axial deformation
- $\delta_{\text{load}} = (PL^3)/3EI$ \hspace{1cm} Eq.2 (deflection of cantilever beam at free end)

Where

- P: applied force
- L: distance from the center of hole to the edge of the crack
- E: Young’s modulus or the slope of stress-strain curve

$$I: \text{moment of inertia of the cantilever beam}$$

$$\delta_{\text{axial}} = P/AE$$ \hspace{1cm} Eq.3 (deformation due to axial loading)

Where

- A: Cross-sectional area
- l: Vertical length of the sample

Slope of the force-deflection curve is given by

$$S = P/\delta$$ \hspace{1cm} Eq.4 (slope of Force vs. Deflection)

Where

- S: Slope of the Force vs. Displacement curve from fracture test

Therefore, total deflection produced by force $P$, on the sample is given by $\delta = P/S$

Substituting in Eq.1

$$P/S = 2[(PL^3)/3EI] + P/AE$$

$$1/S = (2L^3)/3EI + l/A$$

Where

- $a$: length of section
- $b$: width of section
- $h$: height of section

$$E = \frac{S}{(2L^3)/3[(bh^3)/12] + l/A}$$ \hspace{1cm} Eq.5

5. Estimation of Young’s modulus

The force-displacement curves from the PLGA 85:15 samples, prior to degradation and four consecutive days of degradation are shown in Figure 7A. The curves were linearized and shown in Figure 7B. It was evident that as degradation progressed, the curve became steeper while the force required to break the degraded sample decreased.

The slope (S) of the force-displacement curve from each fractured sample was recorded. This slope was used in the derived equation 5 to determine the Young’s modulus at each day of degradation and shown in Figure 8.
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Figure 8 Young’s modulus of PLGA 85:15.

Figure 9 FEA model of PLGA 85:15.

Figure 10 Test vs. FEA result.
6. FEA analysis

3D FEA Models of the specimen with exact dimensions were created for all days of degradation. The hexahedral elements were enriched for XFEM analysis. The specimens were assigned appropriate PLGA 85:15 material properties (Young’s modulus calculated in section 5). The two loading pins were assigned the appropriate steel properties. The steel pins were then inserted in the loading holes to construct a complete assembly as shown in Figure 9.

Element size was kept as low as 0.005 mm in the region of interest (rear of the pre-crack) and the rest of the area was meshed with 3 mm element size. Both steel pins were connected with the specimen via Tie contact algorithm. The bottom pin was held rigidly, arresting all degrees of freedom (DOF).

RESULTS

1. FEA result

Abaqus solver (www.3ds.com) by Dassault Systemes, a commercially available software was used to analyze the samples. The upper pin, as per the ASTM standard, was given a constant velocity of 0.167 mm/sec. The analyses were run until the specimen fractured. The force-displacement curves from each analysis was recorded and plotted against the curves from the physical test and shown in Figure 10.

2. Fracture toughness calculation

Fracture toughness, under mode-I fracture was calculated as per ASTM D5045. A 2D CAD drawing was created and shown in Figure 11.

\[ K_{IC} = \frac{P}{(B \sqrt{W})} f\left(\frac{a}{W}\right) \]  

Where

- \( P \): load at fracture
- \( B \): thickness of specimen
- \( W \): distance from load point to edge of specimen
- \( a \): distance from load point to crack tip

\[ f\left(\frac{a}{W}\right) = \left(\frac{2+a/W}{1-a/W}\right)^{3/2} \left[0.886+4.64(a/W)-13.32(a/W)^2+14.72(a/W)^3-5.60(a/W)^4\right] \]

From figure 11, \( a = 9, w = 18 \). Therefore, \( f(0.5) = 9.51 \)

Calculation of fracture toughness from the force-versus-displacement curve as shown in Fig 12 was followed as per the instruction given in ASTM standard D5045. A tangent line (AB) is drawn on the elastic region of the force-vs.-displacement curve. Then, a 5% greater than line (AB’) was drawn. This line where it intersects the Force-vs.-displacement curve is \( P_0 \). As per the standard, if \( P_{\text{max}} \) falls between lines AB and AB’ then, \( P_{\text{max}} \) should be used for the calculation of trial fracture toughness. If \( P_{\text{max}} \) falls outside the AB and AB’ lines then, \( P_0 \) should be used for calculation of Fracture toughness while the size criteria, \( (W-a)>2.5\left(K_{IC}/\sigma_y\right)^2 \) must be satisfied for test validity to ensure plane strain fracture.

From Figure 12, \( P_0 = 345 \) N

Then, \( K_{IC} \) is found from equation 6 to be 2.8 MPa√m

Similarly, Fracture toughness is calculated for subsequent days of degradation and plotted as shown in Figure 13.

DISCUSSION

In-vitro degradation for Mode I fracture toughness test was conducted on biodegradable polymers. Although discoloration of the samples was seen from first day onward to the final day of the degradation, the chemical effect was not considered in the study. Similarly, the change in molecular weight of sample was also not included in the study. It was observed that the surfaces of the samples became porous as the degradation progressed. The degree of porosity and how much the porosity had pervaded through the depth of the sample, as the degradation progressed, was also not included in the study. The effect of porosity in the sample left was out. This study was conducted purely based on the stress-strain curve.

A simple mathematical relationship between force-displacement curve and Young’s modulus of the material was established, based on the mechanical beam theory. This relationship can be applied to other brittle polymers.

FEA method was successfully implemented at every stage of the
degradation. It is quite an effective tool to solve variety of fracture related issues, such as crack propagation, required fracture force, J-integral, stress-intensity factor (SIF), isochromatic fringes of the stress tensor (Contour plot), animation etc. FEA can substantially save time, money and the laborious work of sample creation. With FEA, repeatability of the result is always possible.

Degradation study showed that on the fourth day of the degradation, the fracture toughness dropped by 45%. This would be very helpful information for the orthopedic doctors while choosing an implant.

Further study should be carried out in other degrading medium such as Phosphate Buffered Saline (PBS) or in-in vivo environment for better understanding for fracture toughness.

The methodology utilized in this research can be used for other brittle polymeric material.

CONCLUSION

It was observed that as PLGA 85:15 degraded, the slope (S) of the force-displacement curve became steeper. Since slope (s) of the force-displacement curve is directly proportional to its Young’s modulus (relationship derived in section 4 under “material and method”), its Young’s modulus increases with the degradation, that is, its resistance to deformation increases. At the same time, its strength, that is, its load bearing capacity decreases.

It was also noted that with the onset of hydrolysis, degradation started and then progressed rapidly. Due to this rapid progression of degradation, PLGA 85:15 became very porous and brittle. Lesser and lesser force was required to fracture the samples as the degradation progressed.

Fracture toughness decreased with the degradation.

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