

# Modeling Changes in the Modulus of Poly( $\epsilon$ -caprolactone) due to Hydrolysis and Plasticization

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**ABSTRACT:** The evolution of the flexural modulus of poly( $\epsilon$ -caprolactone), prepared with a tin(II) 2-ethylhexanoate catalyst, was measured in terms of the polymer molecular weight and moisture content. Changes in the polymer molecular weight were observed, but these did not result in a loss of modulus. Fickian diffusion was used to characterize the absorption of moisture into the polymer. The maximum moisture content and moisture diffusivity constant

of the polymer were determined to be 0.62% and  $2.039 \times 10^{-5} \text{ mm}^2/\text{s}$ , respectively. Reductions in the polymer modulus from 0.5 to 0.4 GPa were attributed to water plasticization. An empirical expression for the polymer modulus as a function of immersion time was developed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3484–3490, 2008

**Key words:** composites; degradation; diffusion; modulus

## INTRODUCTION

Issues with metal medical implants (e.g., stress shielding, growth restrictions) and additional trauma associated with bone grafts has prompted research into new bioresorbable materials for repairing fractured bone.<sup>1–4</sup> Bioresorbable polymers such as poly(glycolic acid) and poly(lactic acid) have been used in the repair of bone fractures, although they have insufficient strength and stiffness to be used alone. As a result, biopolymers such as these are being reinforced with high-particulate reinforcements such as hydroxyapatite<sup>5–8</sup> and Bioglass.<sup>9,10</sup> These composites significantly improve their properties and offer the potential to be used as fracture fixation materials. In addition, efforts have been made to make totally bioresorbable composite materials<sup>11,12</sup> suitable for use in fracture repair. However, a significant drawback of totally resorbable materials is the length of time over which they can retain sufficient strength and stiffness to achieve desired clinical goals.<sup>13</sup> After this time, the material will ideally resorb, returning the fracture site to its natural state without the need for subsequent surgery and leaving no histological or physiological traces.<sup>14–16</sup>

The successful design of resorbable implants requires a knowledge of the material properties that

follow implantation into the human body. To model the evolving properties of a resorbable composite, it is necessary to consider both the constitutive and evolution properties of any interfaces. An *in situ* polymerization method for poly( $\epsilon$ -caprolactone) has been developed for resorbable composites for fracture repair.<sup>17–23</sup> This article details the methods used to characterize the changes in the flexural modulus of poly( $\epsilon$ -caprolactone) in terms of hydrolysis and plasticization as functions of time as a first step to enable improved property prediction for *in situ* polymerized composites.

Poly( $\epsilon$ -caprolactone) is a linear, aliphatic polyester that contains crystalline regions organized into lamellar structures that are interconnected by amorphous regions. The glass-transition temperature for poly( $\epsilon$ -caprolactone) is typically between  $-47^{24}$  and  $-60^\circ\text{C}$ .<sup>25</sup> The polymer was observed by Pitt et al.<sup>26,27</sup> to degrade in two distinct stages. The first stage involves the diffusion of water into the amorphous regions of the polymer, where random hydrolytic scission of the ester bonds causes a reduction in the molecular weight with minimal weight loss from the bulk polymer. The second stage involves weight loss from the amorphous regions and hydrolysis of the crystalline phase.

Jones et al.<sup>28</sup> showed that the brittleness and crystallinity of poly( $\epsilon$ -caprolactone) increase with decreasing molecular weight. The polydispersity of the polymer also affects the rate at which it degrades, with samples containing higher fractions of low-molecular-weight poly( $\epsilon$ -caprolactone) being more susceptible to degradation.<sup>28</sup> This implies that the

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first stage of the degradation process is controlled by the amorphous phase. Therefore, the higher the amorphous polymer content is (and, thus, the higher the molecular weight is), the longer the first stage of the degradation process will last. This long degradation time for high-molecular-weight poly( $\epsilon$ -caprolactone) has been observed by other authors.<sup>29–32</sup>

Expressions to link the flexural and tensile properties of polymers to their molecular weights were developed by Flory,<sup>33</sup> who expanded upon the work of Sookne and Harris.<sup>34</sup> Flory<sup>35</sup> also identified that the changes in the crystallinity of the polymer affect the stress–strain curve. McCormick et al.<sup>36</sup> and Ogawa<sup>37</sup> modified these expressions to include the effects of polydispersity. Golden et al.<sup>38</sup> established that Flory's linear relationship between the polymer strength and molecular weight was only valid up to a critical molecular weight. Above this critical point, the strength is independent of the molecular weight, and the polymer fails in a ductile manner. The modulus, however, is comparatively independent of the molecular weight, with a slight peak attributed to the transition from ductile to brittle behavior. Golden et al.,<sup>38</sup> therefore, concluded that the modulus is independent of the polymer chain length and that flexural testing offers a reliable way to track properties over the ductile-to-brittle transition.

### MODELING THE MOISTURE ABSORPTION

The plasticization of a polymer matrix occurs because of the presence of a solvent (in this case, water) within its structure that allows the chains to move in relation to each other with greater ease. This reduces the stiffness relative to the amount of water absorbed. The absorption of moisture into a homogeneous material can be described with Fickian-based diffusion models.<sup>39</sup> Shen and Springer<sup>40</sup> measured the percentage moisture content ( $S$ ) relative to the initial dry sample mass and found that the maximum moisture content ( $S_m$ ) was dependent on the environmental  $S$ . For a material immersed in a liquid,  $S_m$  is constant. Therefore, the moisture absorbed into a material over time can be estimated by eq. (1) on basis of the following assumptions:<sup>40</sup>

- The material is exposed to the environment from either one or two sides, with both sides being parallel, as shown in Figure 1.
- Initially, both the temperature and moisture distributions inside the material are uniform.
- $S$  and the temperature of the environment are constant.

$$S = G(S_m - S_i) + S_i \quad (1)$$

where  $S_i$  is the initial moisture content of the material;  $S_m$  is the maximum moisture content, which can be attained under the given environmental conditions; and  $G$  is a time-dependent variable, which can be either exactly calculated or approximated as follows:<sup>40</sup>

$$G = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp\left[-(2j+1)^2 \pi^2 \left(\frac{D_x t}{s^2}\right)\right]}{(2j+1)^2}$$

$$G \approx 1 - \exp\left[-7.3 \left(\frac{D_x t}{s^2}\right)^{0.75}\right] \quad (2)$$

where the dummy variable  $s = h$  for a material exposed on two sides and  $s = 2h$  for a material exposed on one side, where  $h$  represents the thickness of the material;  $D_x$  is the diffusivity of moisture in the material in the direction normal to the surface, with the surface assumed to be infinite and the diffusion assumed to be one-dimensional, as defined in Figure 1; and  $t$  is time. Shen and Springer<sup>40</sup> also showed that the diffusivity of a penetrant into a material can be determined from a plot of the percentage moisture absorbed against the square root of time, where the diffusivity of the penetrant into the material is related to the initial linear portion of the curve by

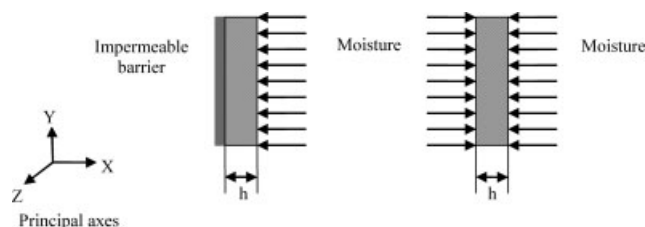
$$\frac{\partial S}{\partial(t^{1/2})} = \frac{4S_m}{h\sqrt{\pi}} \sqrt{D_r} \quad (3)$$

where  $D_r$  is the effective diffusivity of moisture in the polymer. These methods were used by Yoon et al.<sup>25</sup> to determine the moisture absorption characteristics for a range of bioresorbable polymers exposed to humid environments at 36.5 and 45°C. The results in Table I indicate that the degree of crystallization in poly( $\epsilon$ -caprolactone) affected both  $S_m$  and the diffusivity of moisture in to the polymer.

### EXPERIMENTAL

#### Polymer preparation

$\epsilon$ -Caprolactone monomer (Fisher Scientific, Loughborough, UK) was distilled *in vacuo* over calcium hydride (Sigma-Aldrich, Gillingham, UK) immedi-



**Figure 1** Schematic of a material exposed to moisture on either one or two sides.

**TABLE I**  
 **$S_m$  and  $D_r$  Values of Poly( $\epsilon$ -caprolactone) with a Crystallinity of 61.8% at Various Temperatures and Vapor Pressures of Water Across the Whole Polymer as Determined by Yoon et al.<sup>25</sup>**

Temperature (°C)	Property	External pressure of water vapor (atm)			
		0.024	0.042	0.060	0.072
36.5	$S_m$ (%)	0.201	0.335	0.503	0.629
	$D_r$ (cm <sup>2</sup> /s)	$17.35 \times 10^{-8}$	$18.10 \times 10^{-8}$	$19.24 \times 10^{-8}$	$22.90 \times 10^{-8}$
45.0	$S_m$ (%)	0.167	0.259	0.323	0.399
	$D_r$ (cm <sup>2</sup> /s)	$18.86 \times 10^{-8}$	$32.67 \times 10^{-8}$	$40.72 \times 10^{-8}$	$58.09 \times 10^{-8}$

ately before use to ensure low  $S$ . Approximately 80 cm<sup>3</sup> of dried monomer was then transferred to a reaction vessel with a dry nitrogen gas blanket. While it was vigorously stirred, 0.234 cm<sup>3</sup> of the tin(II) 2-ethylhexanoate catalyst (Sigma–Aldrich) was added to the monomer and continuously stirred for another 10 min. The reaction mixture was subsequently drawn up into a syringe and slowly injected into a hot, dry mold to ensure the removal of trapped air. Once the injection process was completed, the mold was sealed and placed into an oven at 120°C for 20 h for polymerization. After this time, the mold was quenched in an ice bath for 20 min before extraction of the plaque and before storage in a vacuum desiccator until it was required.

### Sample preparation and degradation

The 2.4 mm thick polymer plaques were cut with a radial cross cut saw into testing coupons 60 mm long and 15 mm wide that conformed to BS EN ISO 14125 : 1998 (which relates to the determination of flexural properties for fiber-reinforced plastic composites). This standard was used to allow direct comparison with composite samples, not the subject of this article. The edges of the samples were lightly sanded with 600-grit abrasive paper and placed into a vacuum desiccator before degradation and mechanical testing.

Batches of up to six samples were aged in 400 cm<sup>3</sup> of doubly distilled water (DDW) kept in an oven at 37°C for up to 6 weeks. Once the aging period was complete, the samples were either tested wet or transferred to a vacuum desiccator and dried for 48 h before testing.

### Moisture absorption experiments

The moisture absorption in the polymer was measured with a protocol adapted from Shen and Springer.<sup>40</sup> Test samples were dried in a vacuum desiccator and weighed to  $\pm 0.1$  mg. The dried samples were then immersed in DDW at 37°C. Samples were removed at time intervals up to 15 days and quickly blot dried and weighed on an online balance to  $\pm 0.1$  mg before they were returned to the immer-

sion media. Once the samples reached saturation, they were either tested wet or transferred to a vacuum desiccator to dry before testing. Redried samples were weighed to determine the water loss. These measurements were used to determine the fractional  $S$  on the basis of initial dry sample mass.  $S$  was plotted against the square root of the immersion time. The moisture diffusivity constant was subsequently gained from the initial gradient and  $S_m$  from its asymptote with eq. (3).

### Flexural testing

All samples were tested with a three-point bending regime to determine the flexural modulus and strength according to BS EN ISO 14125 : 1998. The flexural testing was performed on a Hounsfield series S testing machine (Salfords, UK). The test span was 45 mm between two support rollers that were 5 mm in diameter. The load was applied through a loading roller that was 10 mm in diameter connected to a 1-kN load cell at a rate of 1 mm/min.

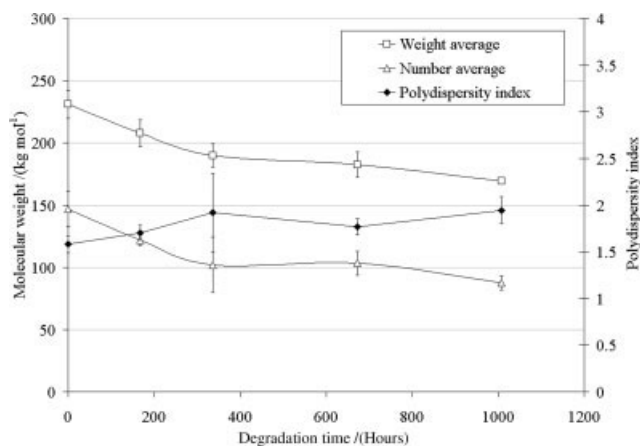
### Gel permeation chromatography (GPC) analysis

The molecular weight of the polymer matrix was determined with GPC. A section of material  $2 \times 2 \times 1$  mm<sup>3</sup> was placed into a clean glass vessel with 2 cm<sup>3</sup> of high-performance-liquid-chromatography-grade chloroform (Fisher Scientific). Samples were analyzed with a Polymer Laboratories GPC system (Church Stretton, UK) with mixed D columns held at 35°C and a refractive-index detector. The mobile phase was high-performance-liquid-chromatography-grade chloroform (Fisher Scientific) at a flow rate of 1.0 cm<sup>3</sup>/min. The system was calibrated with polystyrene standards with elution times between 10 and 17.35 min, which corresponded to molecular weights from 377.4 to 0.580 kg/mol, respectively.

## RESULTS AND DISCUSSION

### Hydrolysis of the polymer

Changes in the molecular weights and polydispersities of the *in situ* polymerized poly( $\epsilon$ -caprolactone) samples are shown in Figure 2. The results indicate



**Figure 2** Changes in the molecular weight and polydispersity of poly( $\epsilon$ -caprolactone) manufactured via the *in situ* polymerization process after immersion in DDW held at 37°C, as determined by GPC. Error bars indicate 1 standard deviation.

that the number-average molecular weight decreased from 150 to 90 kg/mol after 1000 h of immersion. The polydispersity index appeared to increase from 1.5 to 2, as might have been expected from the breakdown of the polymer chains. The weight-average molecular weight of the polymer, which is the product of the number-average molecular weight and the polydispersity index, decreased from 230 to 170 kg/mol.

Batches of *in situ* polymerized samples were tested by three-point bending in both the wet and dry states after immersion. Changes in the polymer flexural modulus were plotted against the respective molecular weights, as shown in Figure 3. The results show that as the molecular weight decreased, the dry flexural modulus was not significantly affected, with a modulus of  $0.50 \pm 0.03$  GPa being maintained throughout the series. The evolution of the wet flexural modulus, likewise, showed no significant change over the molecular weights obtained, with a modulus of approximately  $0.41 \pm 0.02$  GPa observed.

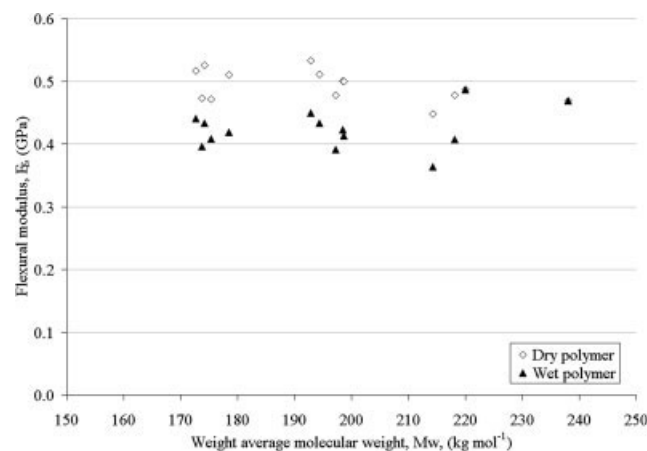
The absence of a significant effect of the molecular weight on the flexural modulus may have been due to the relatively high molecular weight of the initial polymer. Hydrolytic degradation is insufficient to reduce the flexural modulus, which indicates a limiting molecular weight, above which changes in properties will not be observed. However, as the polymer chain lengths decrease further, there will be an expected reduction in mechanical properties. Jones et al.<sup>28</sup> blended high-molecular-weight (50 kg/mol) and low-molecular-weight (4 kg/mol) poly( $\epsilon$ -caprolactone) to reveal reductions in the ultimate tensile strength and elongation as the mean molecular weight decreased and attributed these reductions to

crystallinity-induced embrittlement. However, the results also indicate that the modulus was independent of the polymer molecular weight. These results, coupled with the findings of Jones et al.,<sup>28</sup> suggest that the modulus of poly( $\epsilon$ -caprolactone) remained constant in the range 4–250 kg/mol. Changes in the polymer ultimate tensile strength (UTS) and strain at break were likely to occur below 4 kg/mol, with the modulus decreasing only below a molecular weight of approximately 4 kg/mol.

As moisture penetrates the amorphous regions of the polymer, the hydrolysis of the ester bonds starts to occur.<sup>26,27</sup> This creates a localized acidic environment that subsequently accelerates the degradation of the polymer. This autocatalytic degradation of the polymer will be influenced by the pH of the degradation medium. In the experiments undertaken, DDW was used to determine the effects of moisture alone on the degradation of the polymer. However, within the body, the polymer will be exposed to a buffered aqueous environment that will tend to neutralize any buildup in acid. Phosphate-buffered saline solution or simulated body fluid can be used to replicate this situation, and one would expect the polymer to degrade more slowly.<sup>28–32,41</sup> Hence, the use of DDW represented a worst-case scenario for the degradation of the poly( $\epsilon$ -caprolactone).

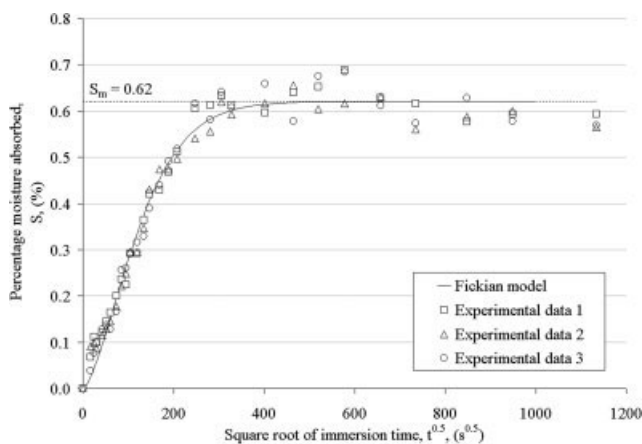
### Moisture absorption

The moisture absorption results, as shown in Figure 4, indicate that the polymer reached an  $S_m$  value of approximately 0.62% after 48 h of immersion. This low level of moisture absorption compared well to those determined by Yoon et al.<sup>25</sup> for poly( $\epsilon$ -caprolactone) exposed to humid environments. No signifi-



**Figure 3** Changes in the flexural modulus versus the molecular weight of tin-catalyzed poly( $\epsilon$ -caprolactone) manufactured with the *in situ* polymerization process for samples tested in the wet or dry state after immersion in DDW held at 37°C.





**Figure 4** Percentage of moisture absorbed versus the square root of the immersion time for poly( $\epsilon$ -caprolactone) manufactured with the *in situ* polymerization process and immersed in DDW:  $S_m$  and the predicted moisture absorption resulted from the Fickian model.

cant difference between the initial dry and redried sample masses was observed in any of the samples tested.

The initial gradient was determined from a line of best fit applied across the data points from 0 and  $150 \text{ s}^{0.5}$ , as shown in Figure 5, and was found to be  $0.0026\%/s^{0.5}$ . The diffusivity constant for moisture into the polymer was then calculated with a simple rearrangement of eq. (3), where  $S_m$  was assumed to be  $0.62\%$  at  $37^\circ\text{C}$  and the average sample thickness was known to be  $2.43 \text{ mm}$ .  $D_r$  of poly( $\epsilon$ -caprolactone) was, therefore, calculated to be  $2.039 \times 10^{-5} \text{ mm}^2/\text{s}$  for a sample immersed in DDW held at  $37^\circ\text{C}$ . This corresponded well to the results of Yoon et al.<sup>25</sup>

With the previously determined  $S_m$  and  $D_r$  for poly( $\epsilon$ -caprolactone) immersed in distilled water at  $37^\circ\text{C}$ , the  $S$  value of the sample at time  $t$  could be recovered with eq. (1), where  $G$  was approximated by eq. (2). A comparison between the theoretical and experimental moisture absorptions of the polymer are shown in Figure 4. The experimental data were generally in good agreement with the theoretical moisture absorption profile generated by eq. (3) and confirmed that the diffusion of water into the polymer was dominated by Fickian diffusion. However, the spread of the data between 15 and 100 h suggested that there may have been some non-Fickian moisture absorption occurring. Although distinguishing this from experimental error was not possible within this study, models to predict non-Fickian moisture absorption in polymers have been developed by a number of investigators, such as Vrentas and Vrentas<sup>42–46</sup> and El Afif et al.<sup>47</sup> These models have predominantly been used for glassy polymers, although Vrentas and Vrentas<sup>42</sup> suggested that these

models could be used to follow the ingress of moisture into both rubbery and glassy polymers. The authors also stated that generally, it is reasonable as an initial step to modeling the moisture ingress to first assume that the entire diffusion process is Fickian.

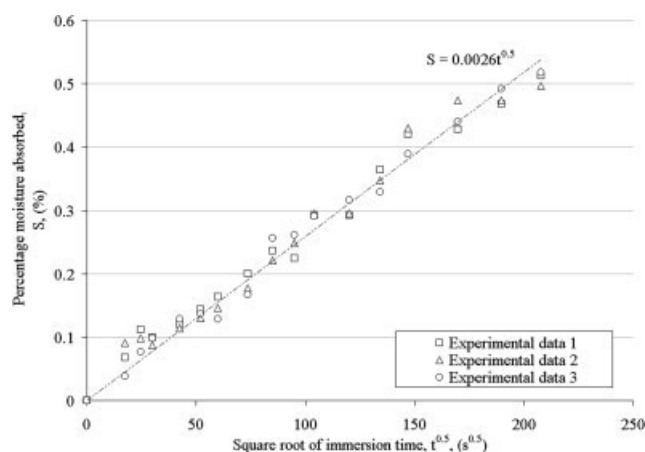
### Predicting polymer plasticization

So the reduction in polymer modulus could be modeled in terms of the polymer  $S$ , the following assumptions were made:

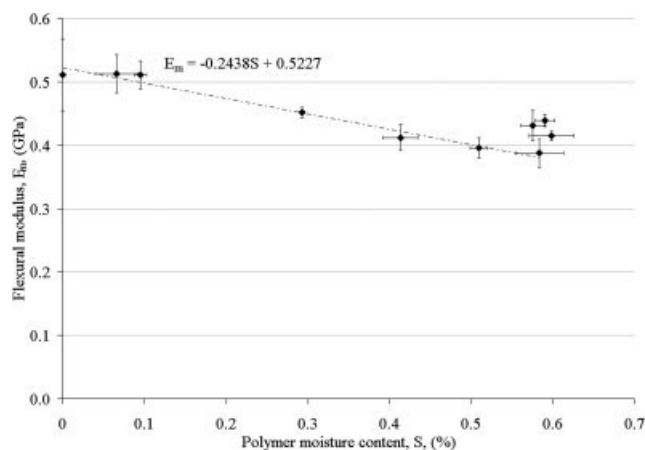
- The effects of plasticization and hydrolysis on the polymer were independent and decoupled.
- Plasticization preceded the hydrolysis of the immersed polymer.
- The reduction in the mechanical properties due to plasticization was immediate and directly proportional to the absorbed  $S$ .

The results presented in Figure 3 show that the modulus of the polymer was reduced by approximately  $0.1 \text{ GPa}$  when tested in the wet state. This reduction was maintained across the molecular weights measured after immersion in DDW. Because the change in modulus was reversible across the range of samples tested, it was probably not related to hydrolysis; this supported the first two assumptions.

The third assumption could be tested via the reanalysis of the results shown in Figure 3, with  $S$  compared to the moduli of the *in situ* polymerized poly( $\epsilon$ -caprolactone) samples immersed in DDW for time intervals ranging from 5 min to 6 weeks, as shown in Figure 6. The results indicate that the polymer modulus decreased linearly as the  $S$  value of the polymer increased toward its maximum value.



**Figure 5** Percentage moisture weight gain versus the square root of the immersion time for *in situ* polymerized poly( $\epsilon$ -caprolactone) immersed in DDW.



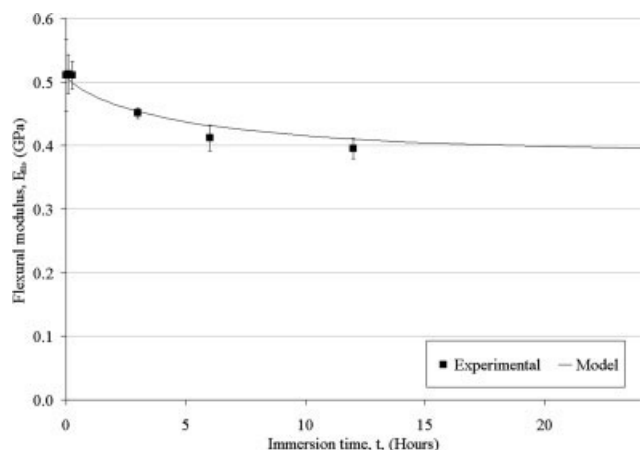
**Figure 6** Relation of the polymer  $S$  to the flexural modulus for *in situ* polymerized poly( $\epsilon$ -caprolactone) immersed in DDW at 37°C for 0–6 weeks. Error bars indicate 1 standard deviation.

This, therefore, validated the assumption that the reduction in polymer modulus was directly proportional to the absorbed  $S$ .

Therefore, the reduced polymer modulus ( $E$ ) could be expressed with eq. (4):

$$E = E_d - (E_d - E_p) \left( \frac{S}{S_m} \right) \quad (4)$$

where  $E_d$  is the initial dry flexural modulus of the polymer,  $E_p$  is the (plasticized) modulus of the polymer at saturation,  $S$  is the moisture content of the polymer at time  $t$  given by eq. (1), and  $S_m$  is the maximum moisture content of the polymer.  $E_d$  was determined from polymer samples dried in a vac-



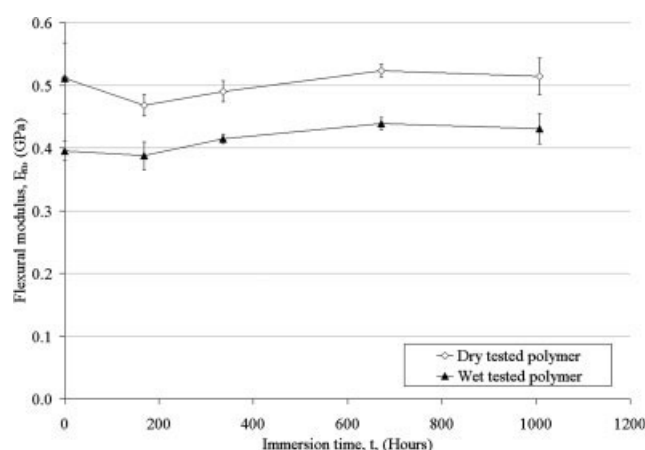
**Figure 7** Evolution of the flexural modulus with the immersion time of the polymer manufactured with the *in situ* polymerization process, immersed in DDW at 37°C, and tested in the wet state. Error bars indicate 1 standard deviation.

uum desiccator for 48 h before testing and determined to be  $0.51 \pm 0.06$  GPa.  $E_p$  was determined from samples that were immersed in DDW between 12 and 168 h and were measured (wet) at  $0.39 \pm 0.02$  GPa.

Equation (4) was used to estimate the modulus due to plasticization, and we compared this (Fig. 7) to the (wet) experimental data from DDW aging. Equation (4) suggests that the polymer became fully plasticized over the first 10–15 h of immersion. The experimental results mirror this decrease in modulus, exhibiting a loss of 0.1 GPa after 10 h of immersion, with an equivalent degradation profile to that described by eq. (4).

The effects of longer term aging on the wet and dry properties of the polymer are shown in Figure 8. Saturation of the polymer with water reduced the modulus by 20% within the initial 15 h of immersion, as previously discussed. After 200 h of immersion, both the wet and dry specimens apparently increased in modulus by 50 MPa, which could have been due to an increase in the degree of crystallinity in the polymer as it degraded. Because this increase was observed in both the wet and dry results, it indicated that the cause was independent of  $S$  and was, therefore, likely to indicate a structural change in the polymer (e.g., an increase in the degree of crystallinity). A difference of 100 MPa was maintained between the wet and dry moduli throughout the period of immersion, which supported the assumption that the effects of plasticization were reversible.

The ability to predict the evolution of the polymer modulus represents a step toward constitutive models for polymer matrix composites. These models will ultimately lead to improved predictions of the



**Figure 8** Evolution of the flexural modulus with the immersion time of the polymer manufactured with the *in situ* polymerization process, immersed in DDW, and tested in either the wet or dry state. Error bars indicate 1 standard deviation.

lifetime of mechanical properties for totally resorbable implants.

### CONCLUSIONS

Our experiments showed that changes in the molecular weight of poly( $\epsilon$ -caprolactone) from 150 to 90 kg/mol due to hydrolysis did not cause significant changes to the wet (0.4 GPa) or dry (0.5 GPa) modulus of the polymer over 1000 h of immersion in distilled water.

Moisture absorption experiments performed upon poly( $\epsilon$ -caprolactone) compared well to those predicted by Fickian diffusion models.  $S_m$  of poly( $\epsilon$ -caprolactone) immersed in distilled water at 37°C was 0.62%, and the moisture diffusion coefficient of the polymer was  $2.039 \times 10^{-5} \text{ mm}^2/\text{s}$ .

The modulus of poly( $\epsilon$ -caprolactone) decreased from approximately 0.5 to 0.4 GPa after 48 h of immersion in distilled water. The model based on  $S$  was in good agreement with the experimental data, which confirmed that the loss of modulus was related primarily to  $S$ .

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