Modelling the evolving ductility of biodegradable polymers

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Postgraduate Modelling Research Group

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Research objective

- Develop a modelling framework for biodegradable polymers;
- For use in the medical device industry, specifically cardiovascular stents
- Overcome risks associated with metal stents
Biodegradable polymers

$\text{H}_2\text{O}$  —  Polymer chain  —  Monomers

Amorphous  
Crystalline  
Semi-crystalline
Experimental observations

Ductile-to-brittle transition for increasing degradation duration in PLA:

![Diagram showing 3-point flexure test](www.substech.com)

- **σ** (Flexural stress, [N/mm²])
- **ε_f** (Flexural strain at failure)
- **E_f** (Flexural strain at failure, [ε_f])
- **Degradation duration**
- **Initial pH 3**
- **Initial pH 7.4**

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Fayolle et al., 2004

\[ M_w (g \text{ mol}^{-1}) \]

\[ \varepsilon_f (\%) \]

\[ \Delta [CO] (\text{mol kg}^{-1}) \]
Fayolle et al., 2004

\[ M_W (g \text{ mol}^{-1}) \]

\[ \xi_f (\%) \]

\[ M_W (kg \text{ mol}^{-1}) \]

\[ \Delta [CO] (\text{mol kg}^{-1}) \]

\[ T = 110^\circ C \]

\[ Time (h) \]
Current work

 Degradation:

- End scissions
- Random scissions

Diagram showing the relationship between molecular weight and the number of molecules, with degradation processes illustrated.
Current work

Degradation:
- End scissions
- Random scissions

Track chain lengths in MATLAB:

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th># of molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td>1020</td>
<td>0</td>
</tr>
<tr>
<td>1040</td>
<td>0</td>
</tr>
<tr>
<td>1060</td>
<td>0</td>
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Current work

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\[
\begin{pmatrix}
1000 & 0 & 0 & \ldots \\
1020 & 0 & 0 & \ldots \\
1040 & 0 & 0 & \ldots \\
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Degradation:

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Current work

Molecular weight

# of molecules

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<tr>
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<td>0</td>
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Molecular weight

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Current work

Molecular weight

# of molecules

Degradation:

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➢ Random scissions

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...
Current work

Track chain lengths in MATLAB:

\[
\begin{array}{ccc}
999 & 0 & 0 \\
1020 & 0 & 0 \\
\textbf{398} & 640 & 2 \\
1060 & 0 & 0 \\
1079 & 0 & 0 \\
\vdots & \vdots & \vdots \\
\end{array}
\]

Degradation:

- End scissions
- Random scissions
Current work

Track chain lengths in MATLAB:

\[
\begin{bmatrix}
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1020 & 0 & 0 & \ldots \\
398 & 640 & 2 & \ldots \\
1060 & 0 & 0 & \ldots \\
1079 & 0 & 0 & \ldots \\
\vdots & \vdots & \vdots & \vdots \\
\end{bmatrix}
\]

Degradation:
- End scissions
- Random scissions

\[M_n \approx \text{time}\]
Predicted stiffness
Relating strain failure to polymer units

Maximum length of extended chain before failure, \( L_f = N \)

Root mean-square end-to-end distance, \( \sqrt{N} = L_0 \)

Strain failure, \( \varepsilon_f \):

Engineering strain:

\[
e_f = \frac{L_f - L_0}{L_0} = \frac{N - N_{\frac{1}{2}}}{N_{\frac{1}{2}}} = \frac{1}{N_{\frac{1}{2}}} - 1
\]

True strain:

\[
\varepsilon_f = \ln(1 + e_f) = \frac{1}{2} \ln(N)
\]

\( N \) = number of polymer units

Freely jointed chain:

- Behaves as entropic spring

\( \varepsilon^M_n \) - related to \( M_n \)

\( \varepsilon^N_n \) - related to chains above \( M_n^{\text{crit}} \)
Results

\[ \varepsilon_f^{\text{Mn}} \]
\[ \varepsilon_f^{\text{N}} \]

Monomers included

Monomers excluded

\[ \varepsilon_f \]

Random:End = 1:10

\[ \text{Random:End} = 1:1 \]

\[ \text{Random:End} = 10:1 \]

\[ \varepsilon_f \times 10^6 \]

\[ \varepsilon_f \times 10^5 \]

Scissions
Results

\[ \varepsilon^\text{M}_f \]

\[ \varepsilon^\text{N}_f \]

Monomers included

Monomers excluded

Random:End = 1:10

Random:End = 1:1

Random:End = 10:1

Scissions

\( \times 10^6 \)

\( \times 10^5 \)

\[ \varepsilon_f \]

\[ M_n \]

\( \times 10^4 \)
Comparing results

Current results:

Fayolle et al., 2004:

\[
\varepsilon_f = M_n^{\varepsilon_{fN}}
\]

\[
\varepsilon_f = M_w^{\varepsilon_{fMn}}
\]

\[
\varepsilon_f (\%) = M_w (kg \ mol^{-1})
\]
Further work

Molecular dynamics

Continuum material models

Continuum device models

Area of interest

Wang et al., 2008:

\[
\frac{\partial M_n}{\partial t} = - \left( k_1 M_n + k_2 M_n C_m^\beta \right)
\]

\[
\frac{\partial C_m}{\partial t} = k_1 M_n + k_2 M_n C_m^\beta + \nabla \cdot (D \nabla C_m)
\]
Further work

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\vdots & \vdots & \vdots & \ldots 
\end{pmatrix}$$

$$\begin{pmatrix}
\varepsilon_f^M_n \\
\varepsilon_f^N
\end{pmatrix}$$
References

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