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# In vivo biostability of polyurethane–organosilicate nanocomposites

Katie E. Styan [a,*,1], Darren J. Martin [b], Anne Simmons [a], Laura A. Poole-Warren [a]

[a] Graduate School of Biomedical Engineering, University of New South Wales, NSW 2052, Australia
[b] Division of Chemical Engineering, School of Engineering, University of Queensland, QLD 4072, Australia

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ABSTRACT

Organically modified layered silicates were incorporated into a polyether soft-segment polyurethane to form composites of at least delaminated morphology. The primary organic modifier was a quaternary ammonium compound; however, one composite included an alternative amino undecanoic acid-modified silicate. The composites' biostability was assessed in an in vivo ovine model over a period of 6 weeks. Attenuated total reflectance–Fourier transform infrared analysis and semi-quantitative scanning electron microscopy image rating indicate a significant enhancement of the base polyurethane biostability with the inclusion of silicate at 3 wt.%. The potential effect at 15 wt.% was confounded by probable leaching of the quaternary ammonium compound affecting the tissue response. The amino undecanoic acid composite compared favourably with the quaternary ammonium compound composite of equivalent silicate loading, and offers the promise of a more favourable tissue response.



## 1. Introduction

Polyurethane (PU) has, historically, been disadvantaged by having poor biostability in vivo. Such degradation is significant as it introduces a risk of loss of device function and/or compromised biocompatibility. Poly(ester)urethanes were among the earliest biomedical PUs. The problem of the ester's hydrolytic instability was initially addressed by poly(ether)urethanes (PEUs), but these have since been shown to be susceptible to degradation via oxidation of the ether linkages [1,2], and are thus currently limited to short-term applications in vivo. A PU originating from past work in our laboratory includes a polydimethylsiloxane (PDMS; $-(CH_3)_3-Si-O-[Si-O-(CH_3)_2]_n-Si-(CH_3)_3-$) soft segment and has significantly increased biostability suitable for long-term in vivo applications [3–5].

A current area of research in our laboratories is organosilicate nanocomposites. Nanocomposites are well represented in the literature and have been the focus of much interest since researchers discovered mechanical property trends that were unique in the field of composites [6,7]. Nanocomposites have been explored predominantly for industrial application, with few studies aiming to exploit the enhancement of mechanical and barrier properties for application in biomaterials. However, increasingly of late, studies have explored the potential of silicates to modulate drug release from hydrogels (e.g. [8,9]).

In the present study, we explore the hypothesized potential of layered silicates in a PEU matrix to mitigate in vivo degradation. Organosilicate nanocomposites have not been assessed in the published literature for in vivo biostability as far as we are aware. Our hypothesis was based on the fact that one layer of montmorillonite (MMT), a commonly used silicate, is 250 nm in two dimensions and 1 nm in the other, giving an aspect ratio of 250 and total surface area of over 700 $m^2 g^{-1}$ [10]. Layers naturally stack in groups on the order of 1000 units, but these can be at least partially delaminated by exploiting the cationic exchange capacity (CEC) of the layered silicate to organically modify the inorganic silicate and increase its compatibility with the organic polymer matrix. It is now well accepted that the dispersed high surface area particles confer barrier effect properties to the polymer. Accordingly, we hypothesized that the included partially delaminated silicate layers would act as a barrier to attack and ingress of degradation species in vivo, thus protecting ether linkages and inhibiting degradation.

## 2. Materials and methods

### 2.1. Poly(ether)urethane

PEU with chemical structure illustrated in Fig. 1 was used in this study. The polymer was supplied by Urethane Compounds (Melbourne, Australia) and contained ~65 wt.% 1000 g $mol^{-1}$ poly(tetramethylene oxide) polyol ether soft segment, 4,4′-diphenylmethane diisocyanate and 1,4-butanediol as the chain extender. The components were combined in the molar ratio 100:7.5:46.3, respectively,

* Corresponding author. Tel.: +61 293853905; fax: +61 296632108.
*E-mail address:* katie.styan@gmail.com (K.E. Styan).
[1] Present address: Commonwealth Scientific and Industrial Research Organisation, Materials Science and Engineering, VIC 3069, Australia.

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