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Title Page

In vitro oxidative degradation of a spinal posterior dynamic stabilisation device

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Abstract

This study quantified the changes of the frequency-dependant viscoelastic properties of the BDyn (S14 Implants, Pessac, France) spinal posterior dynamic stabilisation (PDS) device due to *in vitro* oxidation. Six polycarbonate urethane (PCU) rings and six silicone cushions were degraded by using a 20% hydrogen peroxide / 0.1*M* cobalt (II) chloride hexahydrate, at 37°C, for 24 days. The viscoelastic properties of the individual components and the components assembled into the BDyn PDS device were determined using Dynamic Mechanical Analysis at frequencies from 0.01–30 Hz. Attenuated Total Reflectance Fourier Transform Infra-Red spectra demonstrated chemical structure changes, of the PCU, associated with oxidation while Scanning Electron Microscope images revealed surface pitting. No chemical structure or surface morphology changes were observed for the silicone cushion. The BDyn device storage and loss stiffness ranged between 84.46 N/mm to 99.36 N/mm and 8.13 N/mm to 21.99 N/mm, respectively. The storage and loss stiffness for the components and BDyn device increased logarithmically with respect to frequency. Viscoelastic properties, between normal and degraded components, were significantly different for specific frequencies only. This study demonstrates the importance of analysing changes of viscoelastic properties of degraded biomaterials and medical devices into which they are incorporated, using a frequency sweep.

Keywords: BDyn Implant, Dynamic Mechanical Analysis, Oxidation, Posterior Dynamic Stabilisation, Viscoelastic Properties.

Introduction

Spinal fusion is the gold standard for surgical treatment of low back pain caused by degenerative disorders [(1)–(3)]. Many problems, such as adjacent segment degeneration and pseudarthrosis, are associated with spinal fusion and to alleviate these problems non-fusion techniques have been developed [(4)]. The BDyn device (S14 Implants, Pessac, France) is a posterior dynamic stabilisation device that provides an alternative to spinal fusion. This non-fusion device comprises a mobile titanium alloy rod, a fixed titanium alloy rod, a polycarbonate urethane (PCU) ring and a silicone cushion (figure 1). The BDyn device has been used in the treatment of degenerative lumbar spondylolisthesis [(5)] and an *in vitro* study has shown that the device can successfully limit the range of motion following a laminectomy of L4-L5 segment [(6)].

Since the human lumbar spine has been reported to be resonant between 4–5 Hz in the seated position [(7),(8)], the frequency-dependent viscoelastic properties of the BDyn device, and its elastomeric components, were quantified by Dynamic Mechanical Analysis (DMA) [(9)]. By applying an oscillating force to a multi-component structure and analysing the out-of-phase displacement response, the storage (k') and loss (k'') stiffness were calculated to characterise the viscoelastic properties [(10)]. The storage stiffness represents the elastic portion and it defines the ability of a structure to store energy, while the loss stiffness describes the ability of the structure to dissipate energy through heat and internal motions [(10)]. Lawless et al.[(9)] found that the viscoelastic properties of the BDyn device and its components were frequency dependent, for the frequency range 0.01-30 Hz, and no resonant frequencies were recorded for the device or its components over this frequency range.

The human body is an aggressive environment for biomaterials [11], thus, it is important that the materials of an implant can withstand the environment in the human body and not become degraded to a point where the implant cannot perform its intended function [12]. Orthopaedic implants undergo numerous loads in a cyclical and potentially vibratory manner. Also, implants endure *in vivo* hydrolytic, enzymatic and oxidative degradation at body temperature. Oxidative degradation, the scission of the polymer chains through oxygen [13], has been shown to be an influence in the biodegradation of polyether urethane (PEU) and PCU [14]. PCU has been stated to be more biostable [15] due to the removal of the ether linkages in the soft segment [14],[15].

Numerous studies have used an *in vitro* degradation method, that involves placing the biomaterial into a 20% hydrogen peroxide (H_2O_2) and 0.1*M* cobalt chloride ($CoCl_2$) solution at 37°C [16]–[22], to replicate oxidation. The Haber-Weiss chemical reaction produces hydroxyl radicals from this $H_2O_2/CoCl_2$ solution and it is an appropriate model of the *in vivo* chemical reaction that produces oxygen radicals present at the polymer/cell interface [23]. This *in vitro* method has been shown to reproduce chemical and physical degradation similar to *in vivo* oxidative degradation of PEU and PCU [14],[20]. Further, this *in vitro* $H_2O_2/CoCl_2$ solution has been commonly used to degrade polyether-urethane urea (PEUU), PEU, PCU and silicone modified PEU and PCU [16]–[18],[20],[21]. Many of these studies focus on the degradation of films [16]–[18],[20],[21] or standard tensile specimen shapes [16] to understand how the degradation affects the mechanical behaviour of a material and not how degradation affects polymeric components of implants.

The purpose of this study was to quantify the change in viscoelastic properties, using DMA, of elastomeric components from a BDyn device that have been degraded by *in vitro* oxidation. Furthermore, these components were assembled into BDyn devices and comparisons were made between the degraded elastomeric components and the devices. Comparisons were made between the viscoelastic properties of the normal components [9] and the degraded components.

Materials and methods

Six silicone and six PCU components (figure 2) were obtained from S14 Implants (Pessac, France) and were used for a previous study [9]. These components, which were sterilised with ethylene oxide (EtO) (Steriservices, Bernay, France) for the previous study, were degraded by using a 20% hydrogen peroxide (H_2O_2) and 0.1*M* cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$) oxidative solution. The *in vitro* accelerated ageing of the components was performed at 37°C in a Grant JBN18 water bath (Grant Instruments, Royston, UK). To maintain a relatively constant concentration of radicals, the solution was changed every 3 days and the degradation period lasted 24 days [17],[20]. After the degradation period, the specimens were rinsed with water and were dried in a vacuum chamber (Island Scientific Ltd., Ventnor, United Kingdom) for 48 hours at room temperature.

The viscoelastic properties of the degraded components were measured using a Bose ElectroForce 3200 testing machine running WinTest 4.1 DMA software (now, TA Instruments, New Castle, DE, USA). The DMA technique, machine and software have been used to quantify the storage and loss stiffness of a posterior dynamic stabilisation device, its components [9] and various biological tissues [24],[25].

Similar to the previous study [9], custom-designed grips were used to clamp the titanium alloy rods and/or titanium alloy elastomer housing of the BDyn device. The devices were secured by twelve horizontal screws. The order of component testing was randomised by using the Excel Random Function (Redmond, Washington, USA). The degraded components were then paired randomly and tested in the BDyn device. For testing of the BDyn 1 level, the titanium alloy mobile and fixed rods were gripped. Since the BDyn device is designed to work in both tension and compression, a sinusoidally varying load between +20 N (tension) and -20 N (compression) was applied to the devices. As the components are only loaded in compression, a sinusoidally varying load between -1 N and -20 N (compression) was applied to the elastomeric components. Testing the device and components to these ranges gave a direct comparison between the degraded components, the device and the previous study [9]. Initially, the degraded individual components were tested then the PCU and silicone components were randomly paired, assembled in the BDyn titanium housing and tested. All testing was performed, in air at 37°C ± 1°C, in a custom built chamber in which water was pumped around the chamber while the air temperature was monitored throughout the frequency sweep (figure 3).

The storage and loss stiffness were calculated for 21 different frequencies from 0.01 Hz to 30 Hz; this range is comparable to that of a previous study of the BDyn components [9]. For each frequency (f), a Fourier analysis of the force and displacement waves was performed and the magnitude of the load (F^*), magnitude of the displacement (d^*), the phase lag (δ) and the actual frequency were quantified [9]. The complex stiffness (k^*), storage stiffness (k') and loss stiffness (k'') were then calculated using [9],[26],[27]:

$$k^* = \frac{F^*}{d^*} \qquad (1)$$

$$k' = k^* \cos\delta \quad (2)$$

$$k'' = k^* \sin\delta \quad (3)$$

Attenuated Total Reflectance Fourier Transform Infra-Red (ATR-FTIR) spectroscopy was then performed using a Bruker LUMOS spectrometer (Bruker Optics, Billerica, MA, USA). Spectra were recorded in absorbance mode with a Germanium ATR crystal. Twenty spectra, with a resolution of 2 cm^{-1} between 600 and 4000 cm^{-1}, were acquired and averaged to obtain each spectrum [(28)]. The PCU spectra were normalised to the internal reference 1591 cm^{-1} peak, the C=C bond stretch of the aromatic ring of the hard segment [(20),(29)–(31)], which has been shown to remain unchanged in degradation [(32)].

The surface morphology of the elastomers was examined using the Hitachi TM3030 Scanning Electron Microscope (SEM) (Chiyoda, Tokyo, Japan). Specimens were sputter coated with ~30 nm layer of gold by using an Agar B7340 sputter coater (Agar Scientific, Stansted, Essex, UK). The specimens were examined with back-scatter detector at a 15 keV accelerating voltage.

All statistical analyses were performed using SigmaPlot 13.0 (SYSTAT, San Jose, CA, USA). 95% confidence intervals were calculated (n = 6) and regression analyses were performed to evaluate the significance of the curve fit. Wilcoxon signed rank tests were performed to compare the differences of the components before and after degradation. Whereas a Wilcoxon rank sum test compared the normal BDyn viscoelastic properties [(9)] to the BDyn device assembled with the degraded components. Statistical results with $p < 0.05$ were considered significant.

Results

The ATR-FTIR spectrum, of the PCU and silicone components, is illustrated in figure 4 and figure 5, respectively. Evidence of crosslinking of the PCU has been established as a new absorbance peak was observed at 1174 cm^{-1}. The PCU degraded specimens also showed hard segment degradation with the presence of a new aromatic amine group at 1650 cm^{-1}. There was no evidence of changes to the chemical structure of the degraded silicone specimens (figure 5).

Representative SEM images of the surfaces of the PCU and silicone components are shown in figure 6 and figure 7, respectively. The PCU specimens degraded for 24 days demonstrated surface pitting. There was no evidence of surface pitting, or any other surface morphology changes, with the degraded silicone specimens.

Figure 8 presents the storage stiffness of the (a) BDyn implant, (b) PCU component and (c) silicone component, for normal and degraded components. The mean degraded PCU and silicone components storage stiffness ranged between 87.5 N/mm to 135.3 N/mm and 51.6 N/mm to 60.7 N/mm, respectively. The BDyn implant storage stiffness ranged between 84.46 N/mm to 99.36 N/mm. The storage stiffness logarithmically increased in relation to frequency ($p < 0.05$) (equation 4, where *A* is a coefficient and *B* is a constant, and Table 1).

$$k' = A\ln(f) + B \qquad \text{for } 0.01 \leq f \leq 30 \qquad (4)$$

Figure 9 exhibits the normal and degraded loss stiffness for the (a) BDyn implant, (b) PCU component and (c) silicone component. The degraded PCU and silicone components loss stiffness ranged between 6.03 N/mm to 24.45 N/mm and 4.59 N/mm to 10.83 N/mm, respectively. The BDyn implant loss stiffness ranged between 8.13 N/mm to 21.99 N/mm.

Similarly to the storage stiffness, the loss stiffness logarithmically increased in relation to frequency ($p < 0.05$) (equation 5, where *C* is a coefficient and *D* is a constant, and Table 1).

$$k'' = C \ln(f) + D \qquad \text{for } 0.01 \leq f \leq 30 \qquad (5)$$

For the PCU component, silicone component and BDyn implant assembled with the degraded components, the storage stiffness was larger than the loss stiffness for all frequencies tested. Table 2 provides the frequencies at which the PCU and silicone components were significantly different before and after degradation. The storage and loss stiffness of the silicone component, before and after degradation, were significantly different for the frequency range tested while the PCU component loss stiffness was only significantly different for certain frequencies; 0.5 Hz, 4 Hz to 30 Hz. Also, the storage stiffness of the BDyn device, assembled with degraded components, was significantly different from 0.2 Hz to 20 Hz while, the loss stiffness was significantly different from 0.01 Hz to 0.3 Hz and 0.5 Hz to 15 Hz.

Discussion

This study has quantified the frequency-dependent viscoelastic properties of a posterior dynamic stabilisation device with *in vitro* oxidative degraded components. The degraded components and BDyn device, with the degraded components, were viscoelastic throughout the frequency range tested. The degraded BDyn 1 level device storage stiffness and loss stiffness were less than the storage stiffness (95.56 N/mm to 119.29 N/mm) and loss stiffness (10.72 N/mm to 23.42 N/mm) [9] for the normal BDyn 1 level device. However, the reductions in viscoelastic properties of the PCU and silicone components, due to the in vitro degradation process, are significantly different for specific frequencies. Subsequently, the storage and loss stiffness of the BDyn device assembled with *in vitro* degraded components were lower than those of the untreated device [(9)] only for specific frequencies. These findings demonstrate the importance of analysing changes of viscoelastic properties of specimens over a frequency sweep.

The mean storage stiffness and mean loss stiffness trends of the BDyn device and components followed a logarithmic increasing trend with frequency; these trends are similar to the normal, untreated specimens [(9)]. This is deemed a positive result as the degradation did not affect the frequency-dependant behaviour of the components or device. However, the logarithmic equation coefficients (*A* and *C*) and constants (*B* and *D*) of the degraded specimens were lower than the normal specimens [(9)]. Similarly to the normal BDyn implant and components [(9)], no resonant frequencies were identified for the degraded components and implant with degraded components. Previous studies [(33),(34)] have also shown that the lumbar specimens did not exhibit shock absorbing properties, in pure compression, as no sharp peak detected in the loss modulus for the frequency range [(33)]. Panjabi et al. [(7)] recorded the average *in vivo* lumbar vertebrae resonant frequency at 4.4 Hz for the axial direction, in the seated position. Wilder et al. [(8)] recorded the greatest transmissibility in the male and female lumbar spine of 4.9 Hz and 4.75 Hz, respectively, and also recorded two further resonant frequencies at 9.5 Hz and 12.7 Hz. Any resonance, of the device, at any frequency is a limitation of the device as the resonance may damage the device and in a worst case scenario, the device may fail [(9)].

Other studies have examined the effect of *in vitro* oxidative degradation in relation to tensile strain [(16),(22),(31)] and Dynamic Mechanical Thermal Analysis (DMTA) [(17),(35)], but not DMA. After 36 days of *in vitro* oxidation, Dempsey et al. [(16)] stated that the ultimate tensile strength of Bionate 80A, a PCU, was less when compared to the untreated specimens. However, the ultimate tensile strength of Bionate II 80A was greater for the specimens that were treated; the percentage elongation of Bionate 80A and Bionate II 80A increased by 2-3% after oxidation [16]. Schubert et al. [21] discovered a 10% decrease in stress at high strains of treated PEUU specimens when compared to the untreated PEUU specimens. This result was similar to those of Christenson et al. [20] who found a minor decrease in stress at high strains when comparing the tensile stress-strain behaviour of *in vitro* oxidised PEU and PCU to untreated PEU and PCU. Apart from this decrease in stress, the Young's modulus was unaffected [20]. By using DMTA, Wu et al. [35] investigated the biostability of polyether urethane urea (PEUU) blood sacs and proposed a greater degree of phase separation between hard and soft segments of the implanted sacs due to the α transition shift of -15°C, compared to the control. Hernandez et al. [17] discovered that the maximum loss factor (tan δ), of a PCU, reduced by approximately 0.05 while the storage modulus did not appreciably change after oxidation. From this, the author suggested that there was no significant changes in the hard-soft segment organisation in the bulk [17]. This lack of appreciable change is similar to the present study as the storage stiffness, of the PCU, was not significantly different following degradation over the frequency range tested. However, in the present study, the viscous property (loss stiffness), of the PCU component, was affected by *in vitro* oxidation at 0.5 Hz and from 4 Hz to 30 Hz. This demonstrates the importance of understanding the viscoelastic properties of components and implants in relation to frequency.

Christenson et al. [20] demonstrated that *in vitro* degradation of PEU and PCU, with the 20% hydrogen peroxide (H_2O_2) and 0.1*M* cobalt chloride ($CoCl_2$) solution at 37 °C for 24 days, led to surface pitting and ATR-FTIR spectra changes. Such changes were similar to explanted PCU rods from rabbits after 15 months and PCU specimens from rats after 20 weeks [(31)]. From the ATR-FTIR spectrum, a decrease in absorbance peak intensity at 1247 cm^{-1} was observed for the degraded PCU; this decrease, along with the new absorbance peak at 1174 cm^{-1} provides evidence of chain scission and crosslinking of the soft segment [(17),(20),(36)]. A decrease of the degraded PCU hard segment urethane intensity and a new absorbance peak at 1650 cm^{-1} (the potential degradation product of the aromatic amine[(31)]) provides evidence of hard segment chain scission [(20),(23),(30)]. These spectrum changes are similar to previous work [(20),(30)] however, the new peaks observed at 1174 cm^{-1} and 1650 cm^{-1} are not as prominent as previous studies [(20),(18)] and this may be due to the antioxidant inhibitor used in this commercially available PCU. This inhibitor will have had an effect on the degradation and, in turn, the absorbance peaks at 1174 cm^{-1} and 1650 cm^{-1}. However, the degraded PCU ATR-FTIR spectrum absorbance peaks at 1174 cm^{-1} and 1650 cm^{-1}, from our current study, are similar to another study [(16)] that degraded PCU specimens with an accelerated oxidation method for 36 days. In the present study, SEM images revealed pitting on the surface of the PCU components which has been previously documented for *in vitro* and *in vivo* oxidation of PCU [(16),(31)].

Explanted orthopaedic implants, which contain PCU components, have demonstrated new absorbance peaks at 1650 cm^{-1} and/or 1174 cm^{-1} to demonstrate biological oxidative degradation [(37)–(39)]. However, another explant study did not find new absorbance peaks linked to biological oxidative degradation [(40)]. Ianuzzi et al. [(39)] stated that the majority of the PCU spacers, exhibiting a chemical change associated with biodegradation, experienced this degradation on the surface where the spacer would make contact with tissue. Examination of retrieved PCU spacers revealed that chemical changes were negligible 100 µm below the surface [41]. The elastomeric components of the BDyn device are surrounded by titanium alloy housing (see figure 2). In this study, the components were completely exposed to the $H_2O_2/CoCl_2$ solution without taking into account the effect of the titanium alloy housing. It is hypothesised that the titanium housing will have an effect on the degradation of the polymer components. The titanium alloy housing may protect the components from biodegradation, or alternatively, additional titanium alloy may increase metal ion oxidation (MIO).

Silicone has demonstrated excellent biostability with no identifiable *in vivo* degradation [42] and due to this excellent biostability, silicone has been used to modify PEU and PCU to increase the biostability with the intention to inhibit degradation. The oxidation method, used in this study, has been previously used to understand how degradation affects PCU/PEU [16–18,20,21] and PCU/PEU modified with silicone [18]. In comparison to unmodified PEU and PCU, the percent loss of silicone-modified PEU and PCU soft-segment was less than the unmodified PEU and PCU; this may be an indication of slower rates of crosslinking due to the addition on silicone [18]. The $H_2O_2/CoCl_2$ *in vitro* method has been shown to reproduce chemical and physical degradation similar to *in vivo* oxidative degradation of PEU and PCU [14,20], but not for silicone. It was expected that there would be no significant change in the viscoelastic properties of the silicone cushion, by using this $H_2O_2/CoCl_2$ degradation method. However, the storage and loss stiffness of the treated silicone component was significantly different, for every frequency tested, when compared to viscoelastic properties before degradation. That said, there were no changes evident in the ATR-FTIR spectra and unlike the PCU ring, no pitting or surface morphology changes were observed for the silicone cushions.

As the dynamic stiffness can be affected by load [43], any comparison between different methods and studies must be made with caution [9]. For consistency to our previous study, the methods all remained unchanged with the only change being the degradation of the PCU and silicone components; this was important to understand how the *in vitro* degradation process affects the frequency dependent viscoelastic properties. Regardless, no *in vitro* degradation method fully replicates the biochemical and biomechanical stresses experienced in the body [42]. Consistent with our previous study, the DMA test configuration is not similar to the *in vivo* scenario where the mobile and fixed rods are secured to the pedicles[9]. By securing the mobile rod to the vertebra, an applied load to the device may not displace the two polymer systems equally; hence, the difference in displacement will affect the dynamic stiffness (k^*) and in turn, the storage (k') and loss (k'') stiffness [9]. The BDyn device is designed to allow partial movement along the anatomical planes[9]. This study quantified the viscoelastic properties of the degraded BDyn components, and the degraded components in the device, uniaxially. Rotation of the moveable rod, around an anatomical plane, may affect the response of the out-of-phase displacement to an applied force and hence, affect the viscoelastic properties [9]. However, these limitations do not alter the conclusions of this study because the sinusoidally applied loads ensured a direct comparison between the normal and degraded components and implant.

In conclusion, two viscoelastic components of a spinal posterior dynamic stabilisation device were treated by an *in vitro* oxidation method. Only the PCU components displayed changes to their chemical structure and exhibited surface morphology changes. The loss stiffness, between normal and degraded components, of the PCU component were significantly different for specific frequencies while the storage and loss stiffness of the silicone component were significantly different for all frequencies tested. When compared to the untreated BDyn device, the storage and loss stiffness of the BDyn device assembled with the *in vitro* degraded components were statistically different for certain frequencies. This study demonstrates the importance of analysing changes of viscoelastic properties, of degraded biomaterials, in terms of frequency and medical devices into which they are incorporated, using a frequency sweep.

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Conflict of Interest

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Figure Legends

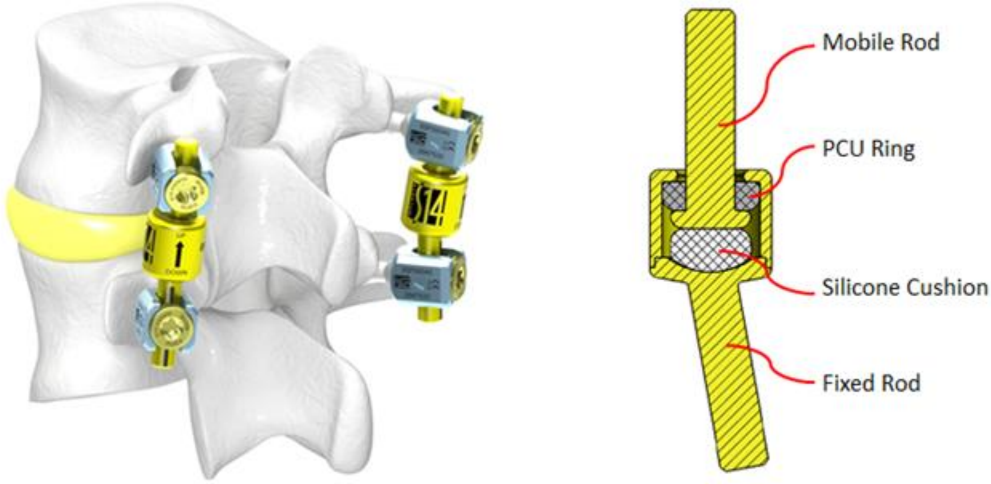

Figure 1: BDyn 1 level device fixed to the vertebrae (Left) [Reproduced with kind permission from S14 Implants, Pessac, France. © S14 Implants] and cross sectional view of the BDyn device (Right). The polycarbonate urethane (PCU) ring and silicone cushion components, along with the mobile and fixed rods, are highlighted.

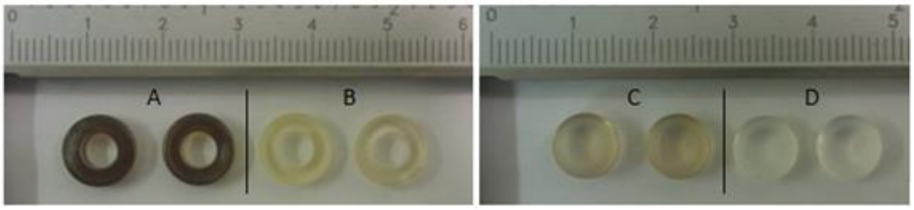

Figure 2: PCU components, (A) before and (B) after degradation, and silicone components (C) before and (D) after degradation. The normal PCU and silicone components are used in the BDyn device.

Figure 3: Testing of BDyn 1 device with degraded elastomer components in the custom built chamber

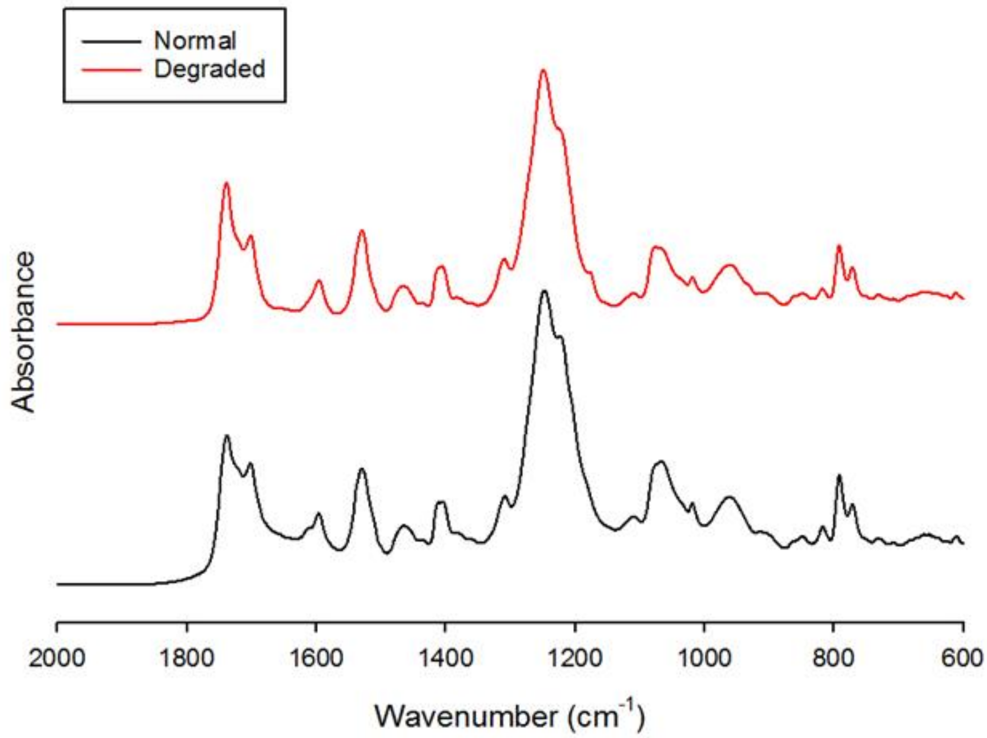

Figure 4: Stacked ATR-FTIR spectra of PCU components before (Normal) and after (Degraded) *in vitro* oxidative degradation

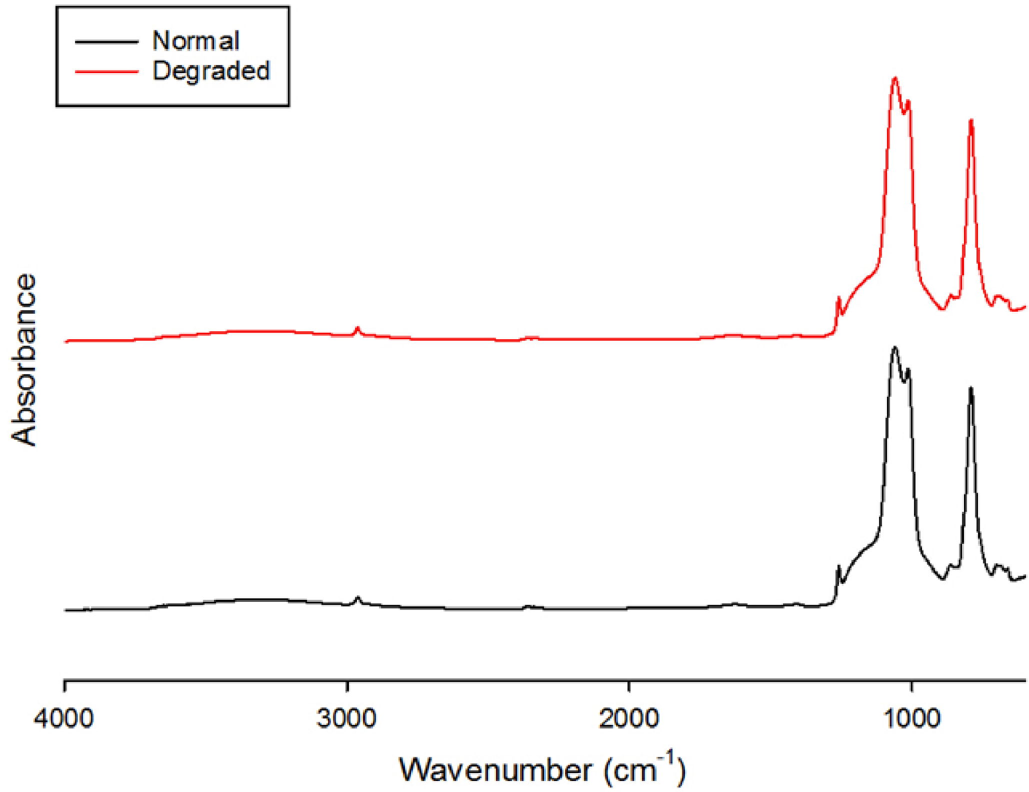

Figure 5: Stacked ATR-FTIR spectra of silicone components before (Normal) and after (Degraded) *in vitro* oxidative degradation

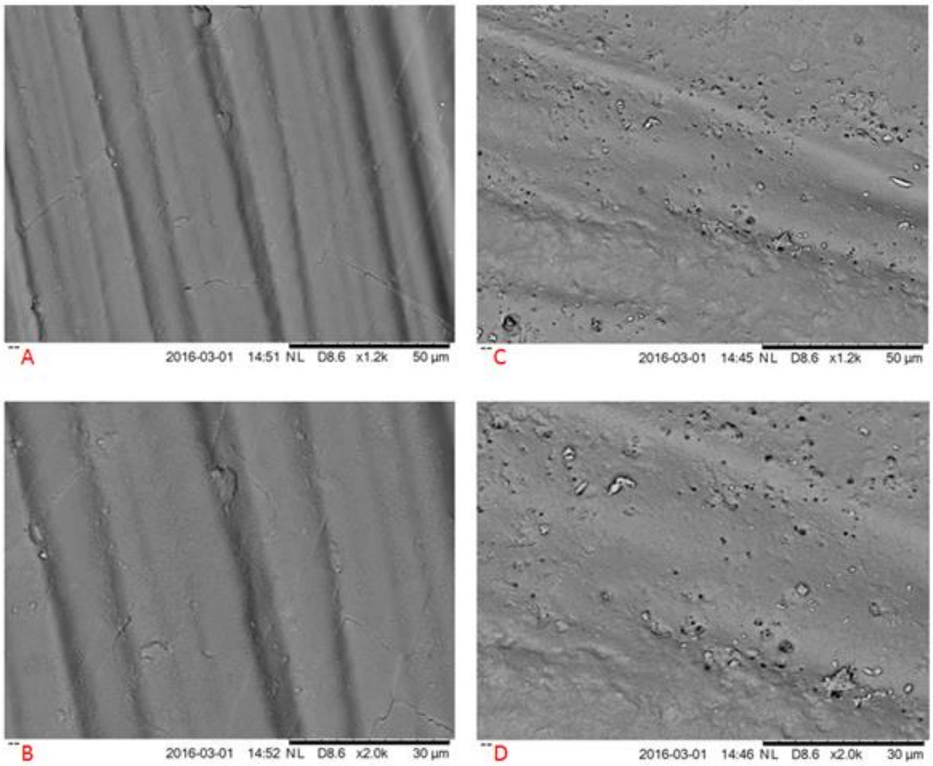

Figure 6: Scanning electron micrographs of PCU components before, at (A) ×1.2k and (B) ×2.0k magnification, and after, at (C) ×1.2k and (D) ×2.0k magnification, *in vitro* oxidative degradation

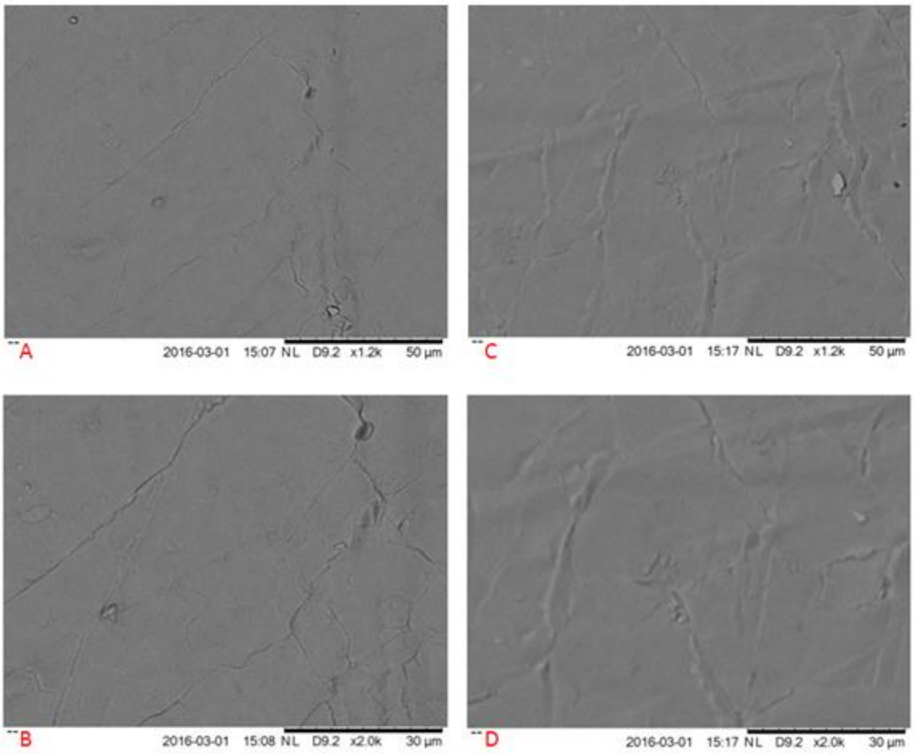

Figure 7: Scanning electron micrographs of silicone components before, at (A) ×1.2k and (B) ×2.0k magnification, and after, at (C) ×1.2k and (D) ×2.0k magnification, *in vitro* oxidative degradation

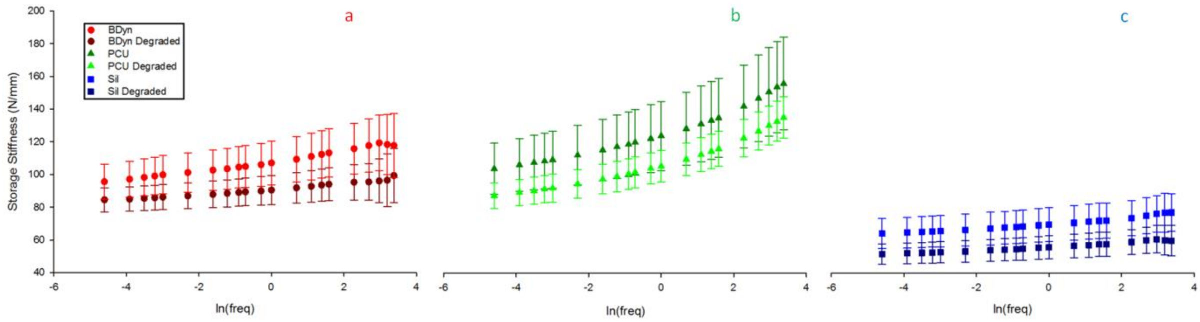

Figure 8: Storage stiffness (k') against ln(f) for (a) normal and degraded BDyn device (BDyn), (b) normal and degraded polycarbonate urethane (PCU) component (PCU) and (c) normal and degraded silicone (Sil) component (mean ± 95% confidence intervals). Normal data is from a previous study [9].

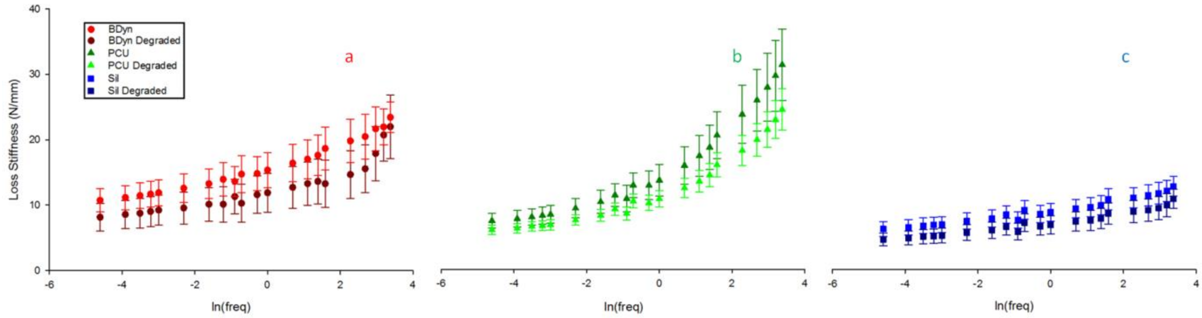

Figure 9: Loss stiffness (*k''*) against ln(*f*) for (a) normal and degraded BDyn device (BDyn), (b) normal and degraded polycarbonate urethane (PCU) component (PCU) and (c) normal and degraded silicone (Sil) component (mean ± 95% confidence intervals). Normal data is from a previous study [9].

Table 1: Storage stiffness (equation 4) and loss stiffness (equation 5) regression analyses of the BDyn devices and its components. Cofficients (*A*, *B*, *C* and *D*) for the individual specimens' storage and loss stiffness (N/mm) trends are provided.

	$k' = A\ln(f)+B$				$k'' = C\ln(f)+D$			
Specimen ID	*A*	*B*	r^2	P Value	*C*	*D*	r^2	P Value
BDyn 1 – 1	2.7	105.1	0.93	<0.001	1.7	16.4	0.90	<0.001
BDyn 1 – 2	1.3	87.0	0.81	<0.001	1.2	11.1	0.80	<0.001
BDyn 1 – 3	1.2	89.6	0.96	<0.001	1.4	14.6	0.81	<0.001
BDyn 1 – 4	0.8	85.1	0.64	<0.001	1.2	11.0	0.82	<0.001
BDyn 1 – 5	3.1	99.4	0.87	<0.001	1.8	15.2	0.80	<0.001
BDyn 1 – 6	1.3	80.3	0.97	<0.001	1.1	8.9	0.77	<0.001
BDyn 1 - Mean	**1.7**	**91.1**	**0.97**	**<0.001**	**1.4**	**12.9**	**0.82**	**<0.001**
PCU – 1	6.3	102.7	0.94	<0.001	2.7	14.3	0.90	<0.001
PCU – 2	6.8	123.0	0.96	<0.001	2.5	14.6	0.89	<0.001
PCU – 3	6.3	118.8	0.96	<0.001	2.3	13.7	0.89	<0.001
PCU – 4	5.2	101.2	0.96	<0.001	1.9	11.3	0.88	<0.001
PCU – 5	5.8	107.5	0.95	<0.001	2.1	12.9	0.89	<0.001
PCU – 6	5.1	101.5	0.96	<0.001	1.9	11.3	0.89	<0.001
PCU – Mean	**5.9**	**109.1**	**0.95**	**<0.001**	**2.2**	**13.0**	**0.89**	**<0.001**
Silicone – 1	1.1	52.5	0.96	<0.001	0.6	6.2	0.93	<0.001
Silicone – 2	1.5	63.7	0.97	<0.001	0.9	9.5	0.96	<0.001
Silicone – 3	0.7	45.3	0.90	<0.001	0.6	6.0	0.90	<0.001
Silicone – 4	1.4	62.2	0.97	<0.001	0.7	7.6	0.95	<0.001
Silicone – 5	1.1	53.4	0.96	<0.001	0.7	6.5	0.93	<0.001
Silicone – 6	1.2	59.4	0.96	<0.001	0.7	7.8	0.95	<0.001
Silicone - Mean	**1.2**	**56.1**	**0.97**	**<0.001**	**0.7**	**7.3**	**0.94**	**<0.001**

Table 2: Wilcoxon Signed Rank test results for the PCU and Silcone components and Wilcoxon Rank Sum test for the BDyn Device. The frequencies stated indicates a significantly different ($p < 0.05$) between the untreated and degraded specimens.

Component	Storage Stiffness	Loss Stiffness
PCU	-	0.5 Hz, 4 Hz to 30 Hz
Silicone	0.01 Hz to 30 Hz	0.01 Hz to 30 Hz
BDyn Device	0.2 Hz to 20 Hz	0.01 Hz to 0.3 Hz, 0.5 Hz to 15 Hz