Effect of accelerated aging on the viscoelastic properties of Elast-Eon™: A polyurethane with soft poly(dimethylsiloxane) and poly(hexamethylene oxide) segments

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ABSTRACT

The viscoelastic properties of cylinders (diameter 5 mm, height 2.2 ± 0.2 mm) of Elast-Eon™ 3, (a polyurethane with poly(dimethylsiloxane) and poly(hexamethylamine oxide) segments) were investigated before and after the specimens had undergone accelerated aging in saline solution at 70 °C for 38, 76 and 114 days (to simulate aging at 37 °C, for 1, 2 and 3 years, respectively). All sets of specimens were immersed in physiological saline solution at 37 °C during testing and the properties were measured using dynamic mechanical analysis (DMA). A sinusoidal cyclic compression of $40\,N \pm 5\,N$ was applied over a frequency range, f, of 0.02–100 Hz. Values of the storage, E', and loss, E'', moduli were found to depend on f; the dependence of E' or E'' on the logarithm (base 10) of f was represented by a second-order polynomial. After accelerated aging, the E' and E'' increased significantly ($p < 0.05$) and the specimens became darker and more opaque. SEM images showed that accelerated aging affected the surface morphology but ATR-FTIR spectra did not show any appreciable change in surface chemistry. DSC thermograms showed some slight changes in thermal properties following accelerated aging.

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1. Introduction

A polyurethane with soft segments of poly(dimethylsiloxane) (PDMS) and poly(hexamethylene oxide) (PHMO) (Fig. 1) has been synthesised as an alternative to silicone elastomers for surgical implants and is marketed under the name Elast-Eon™ [1,2]. Recently, it has been suggested that Elast-Eon™ could be used in flexible artificial joints for the fingers and wrist [3], which at present, are made from medical grade silicone elastomers, but suffer from high fracture rates [3–7]. It has also been suggested [2,3,8] that the advantages of Elast-Eon™ over silicone elastomers, which include improved tensile strength and tear resistance, make it favourable as a possible substitute for silicone elastomers in finger and wrist implants. Furthermore, it has been proposed that the chemical stability of Elast-Eon™ in biological fluids [8–10] may lead to the avoidance of silicone synovitis [11,12], another complication associated with silicone elastomer implants [3]. Other medical applications of Elast-Eon™ and polyurethanes include cardiovascular applications, catheters and reconstructive surgery materials [1,2,13,14].

The viscoelastic properties of an elastomer are important in a flexible joint to ensure that it has the required stiffness and recoils, after a force is removed, in a reasonable time [15,16]. These properties (including creep, stress relaxation and hysteresis) can be defined by the values of two parameters: the storage, E', and loss, E'', moduli [17,18]. E' represents the elastic response of the material, where the work done in deforming the material is stored as potential energy that is subsequently used for recoil [17,18]; E'' represents the viscous response of the material, where the energy supplied to the material is dissipated [17,18]. These two parameters are related to the Young's modulus, E^*, of a viscoelastic material by ($E^* = \sqrt{E'^2 + E''^2}$) [16,17].

For silicones, E', E'' and E^* may depend on the frequency, f, at which a force is applied [15,16,19], so their frequency dependence also needs to be determined for Elast-Eon™. The theory of elasticity of elastomers is sufficiently complicated that the values of E' and E'' are not readily relatable to the chemical structure of the polymers [20,21]; for most purposes, they are best regarded as empirical properties of the bulk material [22].

The properties of materials that are suitable for implantation in the body should not deteriorate unacceptably during their shelf-life or during the time that they are implanted [23]. Elast-Eon™ has been implanted into sheep, [9,10] but the implantation times were short compared with those of implants that are intended to remain in the body for many years [3,7]. The performance of implant materials can also be determined by retrieval studies of implants that have failed in

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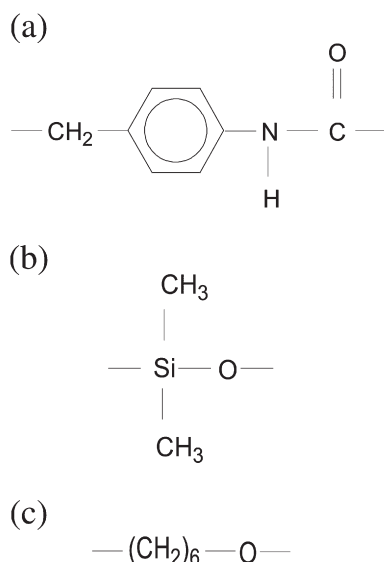*E-mail address:* a.mahomed@bham.ac.uk (A. Mahomed).

(a)

(b)

(c)

Fig. 1. Structural formulae for repeating monomer units in (a) polyurethane, (b) poly (dimethylsiloxane) (PDMS) and (c) poly(hexamethylene oxide) (PHMO) [1,48].

the human body [24]. However, a material needs to be investigated *in vitro* before it can be implanted [25].

The problem that then arises is that studies that correspond to the projected life of an implant material in the human body (perhaps of the order of 20 years) are not feasible; the conventional way of overcoming this problem is to subject materials to elevated temperatures, known as "accelerated aging" [23,26]. Aging of a material can be accelerated by a factor of $2^{\Delta T/10}$ by increasing the temperature by an increment ΔT [23,26]. Therefore, maintaining a material at 70 °C for 38 days is equivalent to aging it for $38 \times 2^{(70-37)/10} = 380$ days, or just over 1 year, at 37 °C.

Accelerated aging of Elast-Eon™ (70 °C for 2 weeks, equivalent to 20 weeks at 37 °C) showed that degradation and surface cracking occurred in material that had been sterilised by autoclaving but not in material that had been sterilised by ethylene oxide or γ-irradiation [27].

No *in vitro* test can completely mimic the conditions in the human body; such tests are intended to ensure that there are no obvious hazards before a material is incorporated in a device for clinical trial [25]. The assumption underlying accelerated aging is that the degradation of a polymer follows first order kinetics and that the elevated temperature does not induce any chemical changes or phase transitions that would not have occurred at 37 °C [23]. Therefore, Elast-Eon™ was investigated, before and after accelerated aging, to determine what other changes could have taken place. Differential scanning calorimetry (DSC) was used to characterise the thermal properties since, like, viscoelastic properties they are characteristic of the bulk material [28]. Scanning electron microscopy (SEM) was used to detect any obvious changes to the morphology of Elast-Eon™ at a microscopic level; however, since it provides information about surfaces [29], the results cannot be simply related to any changes in E' and E''. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy [30] was used to detect changes in the surface chemical structure that might be associated with any morphological changes detected by SEM. However, the main purpose of this paper is to determine the viscoelastic properties of Elast-Eon™ before and after accelerated aging.

2. Materials and methods

2.1. Materials

Elast-Eon™ 3 was supplied by the manufacturer (AorTech Biomaterials Pty Ltd., Frenchs Forest, Australia) as cured cylinders of material, for previous work, in 2002 [3]; its properties are listed in

Table 1. It was then stored in air, at room temperature, in the dark, until 2007. The original cylinders were cut into six cylindrical specimens (diameter 5 mm, height 2.2 ± 0.2 mm), for the experiments reported here, using a Colchester 5*20 Chipmaster lathe (Rockwell Machine Tools Ltd., Redditch, B98 7SY, UK). The resulting test specimens complied with the aspect ratio in British Standard BS 903-A6:1992 [31] for compression testing of rubber specimens. This is important for elastomers because the ratio of the radius to height of cylindrical specimens strongly influences the results [15,32].

2.2. Testing environment

Six specimens were tested, one at a time, in a cell containing physiological saline solution (9.5 g L^{-1} of sodium chloride in deionised water) surrounded by a circulating water jacket at 37 °C, to simulate *in vivo* conditions, as in previous work on silicone elastomers [15,19]. Testing did not begin until the temperature of the physiological saline solution was stable at 37 °C.

2.3. Measuring viscoelastic properties

The same testing equipment and protocol were used in this investigation as described in work on silicone elastomers [15,19]. A mechanical testing machine (ELF 3200, BOSE Corporation, ElectroForce Systems Group, Minnesota, USA) with a 225 N load cell (nominal precision ± 0.005 N) was used to carry out all the tests.

Preliminary experiments showed that the load/deformation curves had a linear portion centred around a static load of 40 N. Therefore, the six specimens were subjected to sinusoidal cyclic compression tests, oscillating 5 N either side of a load of 40 N over a frequency range of 0.02–100 Hz at 22 different frequencies. Four sinusoidal cycles were applied between 0.02 and 0.5 Hz. Above 0.5 Hz the number of cycles increased with the frequency, under the control of the standard machine software, reaching a maximum of 625 cycles at 100 Hz. All the tests were controlled using the WinTest DMA software (BOSE Corporation, ElectroForce Systems Group, Minnesota, USA). Once a test started, the system ramped the load to 40 N and held it there for 5 s to allow for any creep to occur before testing.

Once the dynamic cycling had begun, the specimen was pre-cycled for 5 s to allow for specimen stabilisation before data were taken. Therefore, a 10 second rest period was allowed between each dynamic loading cycle, for the specimen to recover. These times were chosen after preliminary testing showed that they were adequate to obtain reproducible results.

2.4. Accelerated aging

Six specimens were aged by immersing them in physiological saline solution and placing them in a Carbolite natural convection laboratory oven (Carbolite, Hope Valley, S33 6RB, UK) at 70 °C for 38, 76 and 114 days, which is equivalent to aging at 37 °C for 1, 2 and

Table 1
Summary of the properties of Elast-Eon™ 3 supplied by the manufacturer (AorTech Biomaterials Pty Ltd., Australia). Results were obtained from compression moulded sheets, conditioned at ambient conditions for a minimum of 7 days.

Property/test	Test method	Result
Durometer hardness[a]	ASTM D2400	78A
Tensile strength (MPa)	ASTM D638	18
Tensile stress at 100% strain (MPa)	ASTM D638	5
Tensile strain at break (%)	ASTM D638	630

[a] Durometers are commonly used to measure the hardness of an elastomer by applying a force to the material and measuring the resulting indentation depth in the material [49–53]. A Type A durometer is used on softer materials such as elastomers [49–51,53,54].