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Effect of Accelerated Aging on the Viscoelastic Properties of a Medical Grade Silicone.

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Abstract

The viscoelastic properties of cylinders (diameter 5 mm, height 2.2 ± 0.2 mm) of Nagor silicone elastomer of medium hardness, 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 ± 5 N was applied over a frequency range, *f*, of 0.02-25 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''* values of did not increase significantly ($p < 0.05$). Furthermore, scanning electron microscopy (SEM) showed that accelerated aging did not affect the surface morphology of silicone. Attenuated total reflectance Fourier transform infra-red spectroscopy (ATR-FTIR) showed that accelerated aging had a negligible effect on the surface chemical structures of the material. Differential scanning calorimetry (DSC) showed no changes to the bulk properties of silicone, following accelerated aging.

Keywords: Accelerated aging; compression; dynamic mechanical analysis (DMA); silicone; viscoelasticity.

1. Introduction

The properties of materials such as silicones (PDMS) that are suitable to be implanted in the body [1-3] should not deteriorate unacceptably during their shelf-life or while *in vivo* [4]. One method that can be used to study the aging properties of a material is to implant it into animals [5-8] or by retrieval studies of implants that have failed in the human body [9]. However, implantation and retrieval 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. Another method that can be used to determine whether deterioration is likely to occur over long time scales, is to subject materials to elevated temperatures, known as "accelerated aging" [4, 10]. Aging of a material can be accelerated by a factor of $2^{\Delta T/10}$ by increasing the temperature by an increment ΔT [4, 10]. Therefore, maintaining a material at 70^{o}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^{o}C. This is particularly useful for studying the aging of materials that are being considered for implantation.

A previous study [11] measured the Young's modulus (given by $E^* = \sqrt{E'^2 + E''^2}$) of Elast-Eon™ 3, (a polyurethane with poly(dimethylsiloxane) and poly(hexamethylamine oxide) segments) before and after accelerated aging, using the same technique described in this study. 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 [12, 13] ; E'' represents the viscous response of the material, where the energy supplied to the material is dissipated [12, 13]. The purpose of this paper, is to measure the storage, E', and loss, E'', moduli, as a function of frequency, f, in compression, before and after accelerated aging, of a

silicone elastomer (Nagor) and compare it to the results obtained for the polymer Elast-Eon™ 3 (a polyurethane containing PDMS segments) [11]. Silicone was used for comparison with Elast-Eon™ because it is also used in similar biomedical applications.

In addition, scanning electron microscopy (SEM) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) were used to assess the changes in the surface chemical structure and morphology of the material, before and after accelerated aging. Differential scanning calorimetry (DSC) was used to characterise the thermal properties of the material in order to monitor changes in the properties of the bulk material.

2. Materials and Methods

2.1 Materials

Nagor silicone of medium hardness (with a Durometer Hardness Type A minimum value of 18 and maximum value of 23; values obtained from the manufacturer, Nagor Limited (Cumbernauld, Glasgow, G68 9HN, UK)) was supplied as cured rectangular blocks. The original blocks were cut into six cylindrical specimens (15 mm diameter, 6mm height complying with the standard for the aspect ratio in compression tests [14-16]), for the experiments reported here, using a Colchester 5*20 Chipmaster lathe (Rockwell Machine Tools Ltd, Redditch, B98 7SY, UK).

2.2 Testing environment

The 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, 16]. Testing did not begin until the temperature of the physiological saline solution and silicone was stable at 37°C, which took approximately 30 minutes.

2.3 Measuring viscoelastic properties

The same testing equipment and protocol were used in this investigation as described in work on silicone elastomers [16] and Elast-Eon™ [11]. 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 specimen 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- 25 Hz, at 19 different frequencies. Four sinusoidal cycles were applied between 0.02-0.5 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 175 cycles at 25 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 seconds to allow for any creep to occur before testing.

Once the dynamic cycling had begun, the specimen was pre-cycled for 5 seconds 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 Effect of accelerated aging

Six specimens of the silicone elastomer 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 3 years, respectively. After 38, 76 and 114 days, the viscoelastic properties were measured using the same procedure described above. The specimens were aged using exactly the same procedure as a previous study of Elast-Eon™ 3 [11], to enable the results of the two studies to be compared.

2.5 Statistics

Mean values and standard deviations for E' and E'' were calculated at each value of f, from the six measurements taken for each specimen. Results were plotted against the logarithm (base 10) of f, measured in Hz and second order polynomials fitted to give a smooth representation of a line through the data points [15, 16]. The results before and after accelerated aging were compared by calculating the upper and lower 95% confidence intervals [15, 16]. These intervals represent the regions in which there is a 95% probability of finding the true mean value [15, 16]. If the upper and lower 95%

confidence intervals do not overlap, the probability, *p*, that they are not different is less than 0.05 [17].

2.6 Scanning electron microscopy

Specimens of Nagor silicone (before and after accelerated aging) were coated with platinum and examined by SEM, (FEI/Philips XL30 ESEM-FEG, FEI, Hillsboro, Oregon 97124, USA) at magnifications in the range ×100 to ×10000.

2.7 ATR- FTIR

ATR-FTIR was used to study the changes in the surface chemical structure of the specimens, before and after accelerated aging. The analysis was performed on a Nicolet Magna-IR 680 Fourier transform infrared spectroscope with OMINIC software on the computer interfaced to the spectrometer (Thermo Fisher Scientific UK Ltd., Loughborough, Leicestershire, LE11 5RG, UK). The spectra were recorded in the wave-number range 600-4000 cm^{-1}, before and after accelerated aging and compared. The spectra peaks were assigned by consulting the literature [5, 8, 18].

2.8 Differential scanning calorimetry

A Mettler Toledo DSC 821e (Mettler-Toledo Ltd, Leicester, LE4 1AW), equipped with a liquid nitrogen cooling accessory for sub-ambient cooling was used to obtain thermograms. The specimens were cycled in sealed aluminium pans.

DSC was conducted over a temperature range of -150 to 60°C, at a constant heating rate of 10°C/min on the specimens of Nagor silicone (before and after accelerated

aging). The specimens were first quench-cooled to the start temperature of -150°C. Air was used as the reference material in the empty pan. The T_g (glass transition temperature) and the T_m (highest temperature at which crystallinity can still be detected or peak of an endothermic process) of the materials, were measured [18-21].

3. Results

3.1 Effect of frequency on the viscoelastic properties of Nagor silicone elastomer

In Figure 1, both *E'* and *E''* clearly demonstrated frequency-dependent behaviour. In Figure 1a, *E*' increases slowly up to a log*f* value of -0.125, (corresponding to $f \approx 0.75$ Hz). After this point, *E*' increases more steeply. Similarly, the *E''* is fairly constant until a log*f* value of -1.22 (corresponding to $f \approx 0.06$ Hz) and then increases rapidly.

3.2 Effect of accelerated aging of Nagor silicone elastomer

The results demonstrated that the properties of the silicone specimens, were not significantly affected by accelerated aging (in physiological solution at 70°C for 38, 76 and 114 days). Figure 1a shows the 95% confidence intervals, for *E'* before and after accelerated aging for Nagor silicone cylinders plotted against the $\log_{10}$ of loading frequency, *f*. Similar graphs are shown for *E''* in Figure 1b. The confidence intervals overlapped throughout the frequency range, i.e. accelerated aging had no significant effect on *E'* and *E''* values. Accelerated aging did not change the appearance of the specimens.

3.3 Scanning electron microscopy

Comparison of Figures 2a and b shows that accelerated aging did not have an appreciable effect on the surface morphology of the silicone.

3.4 ATR- FTIR

The ATR-FTIR spectra for the Nagor silicone specimens, before and after accelerated aging, are shown in Figure 3. The peak wave-numbers are shown in Figure 3 and the peak assignments are shown in Table 1. The spectra obtained before and after accelerated aging were almost identical, with very slightly increased peak heights, for the aged specimen, at wave-numbers of 792, 1009 and 1062 cm^{-1}.

3.5 Differential scanning calorimetry

The DSC thermograms for the specimens of Nagor silicone, before and after accelerated aging, are shown in Figure 4. The thermograms for, before and after aging, are almost identical, and quantitative results in Table 2 show the glass transition, T_g, and, endothermic peak, T_m, temperatures obtained from the thermograms [18-21]. For the Nagor silicone specimens, the results show that the T_g and T_m values were unchanged by accelerated aging.

4. Discussion

For the Nagor silicone cylinders, the *E'* and *E''* demonstrated frequency-dependent behaviour, which is consistent with those obtained for other medical grade silicone cylinders [15, 16]. This seems to be in general agreement with previous studies [22-28] that, accelerated aging of silicone is not likely to cause the silicone to degrade or greatly affect its viscoelastic properties or change its appearance. A study [29] also concluded that the appearance of two silicones for dental liners, Molloplast-B and Silastic 390, did not change after being immersed in water at 37°C for six months.

On the other hand, the Elast-Eon^{TM} cylinders [11], that was treated in exactly the same way as Nagor silicone cylinders, showed changes in viscoelastic properties (both *E'* and *E''* increased significantly after aging) and in appearance (darker and more opaque) as a result of accelerated aging, at 70^{o}C. Both storage, *E'*, and loss, *E''*, moduli of Elast-Eon^{TM} depended on the frequency, *f*, at which it was loaded [11].

DSC shows that accelerated aging does not appear to have an effect on the thermal properties of Nagor silicone. However it has been reported that the thermal effects of Elast-Eon^{TM} 3 were affected by aging [11]. SEM shows that accelerated aging did not affect the surface morphology of silicone. Similarly, ATR-FTIR spectroscopy shows that accelerated aging had a negligible effect on the surface chemical structures of the material. This observation was also reported for Elast-Eon^{TM} 3 [11]. Any surface changes will have a negligible effects on *E'* and *E''*, since their values are dominated by the behaviour of the bulk material. However, increased roughening could affect the failure of the material by introducing stress concentrations which could induce crack propagation.

5. Conclusions

The main conclusions from this study are summarised below.

- Storage, *E',* and loss, *E''*, moduli of Nagor silicone elastomer depended on loading frequency, *f*, regardless of whether or not accelerated aging had occurred.
- Accelerated aging (at 70^{o}C) led to little change in surface chemical structure of Nagor silicone elastomer when monitored by ATR-FTIR. DSC indicated no change in the thermal properties after accelerated aging. SEM indicated that accelerated aging did not affect the surface morphology of the silicone.
- Accelerated aging (at 70^{o}C) did not change the appearance of Nagor silicone and did not significantly ($p < 0.05$) increase the *E'* and *E''* values.
- In contrast to the results of the Elast-Eon™ 3, that acted as a comparison, the results demonstrated that the viscoelastic properties and appearance of the silicone specimens, were not significantly affected by accelerated aging (in physiological solution at 70°C for 38, 76 and 114 days).

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Table 1: The peak assignments for the ATR-FTIR spectra, shown in Figure 3, are tabulated here. The spectral peaks were assigned by consulting the literature [5, 8, 18].

Peak wave numbers (cm^{-1})	Proposed peak assignment
3318	O-H stretch
2958	C-H stretch in CH_3 bend
1704	C=O stretch
1529	N-H bend and C-N stretch
1257	Si-CH_3 stretch
1065	Si-O-Si stretch
1016	Si-O-Si stretch
792	$(Si\text{-}CH_3)_2$ stretch

Table 2: T_g and T_m measurements obtained using DSC for Nagor silicones

	T_g (°C)		T_m (°C)	
	Onset	Midpoint	Onset	Midpoint
Before aging	-123.93	-120.90	-50.04	-42.34
After aging	-124.72	-120.81	-50.37	-41.83

Figure Captions

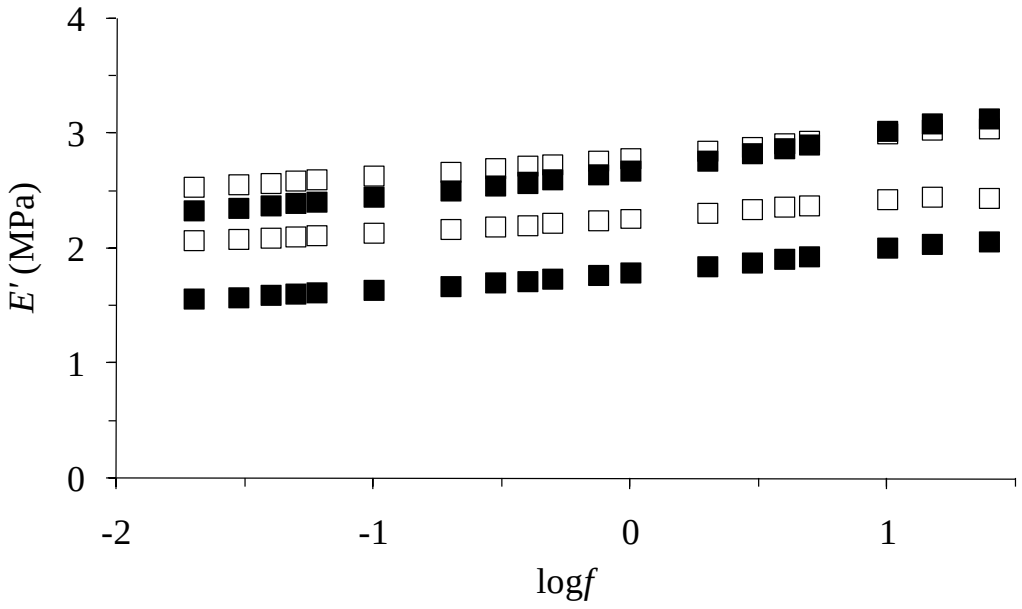
Fig. 1 Upper and lower 95% confidence intervals of (a) storage modulus, *E'*, (b) loss modulus, *E''*, plotted against the logarithm (to the base 10) of loading frequency, *f*. Results are given for Nagor silicone specimens before (■) and after (□) accelerated aging (in physiological solution at 70°C for 114 days).

Fig. 2 SEM (magnification x 10000) of Nagor silicone (a) before (—) and (b) after (– · –) accelerated aging.

Fig. 3 ATR-FTIR spectra of Nagor silicone before (—) and after (– · –) accelerated aging. The peak wavenumbers are shown in this figure and the peak assignments of the wavenumbers are shown in Table 3.

Fig. 4 DSC thermograms of Nagor silicone before (—) and after (– · –) accelerated aging.

Fig. 1



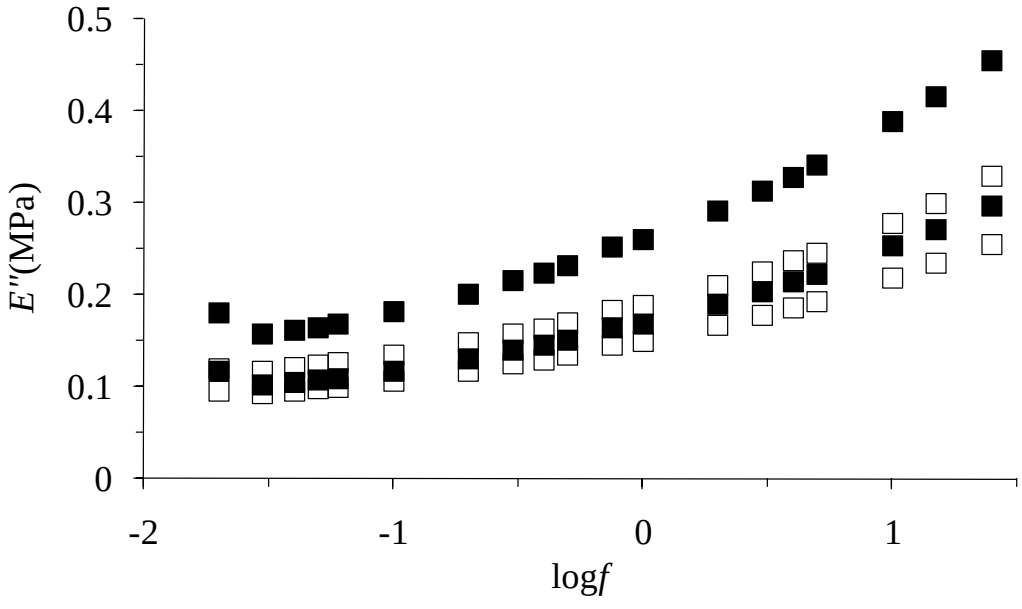


Fig. 2

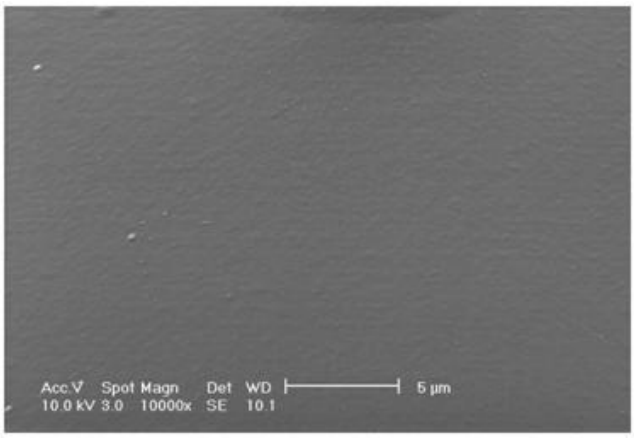


Fig. 2a

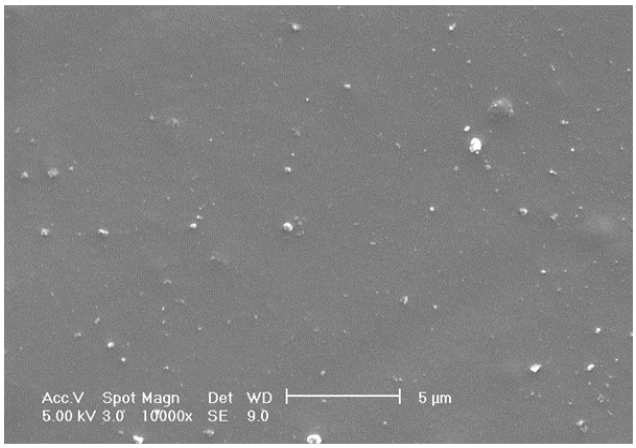


Fig. 2b

Fig. 3

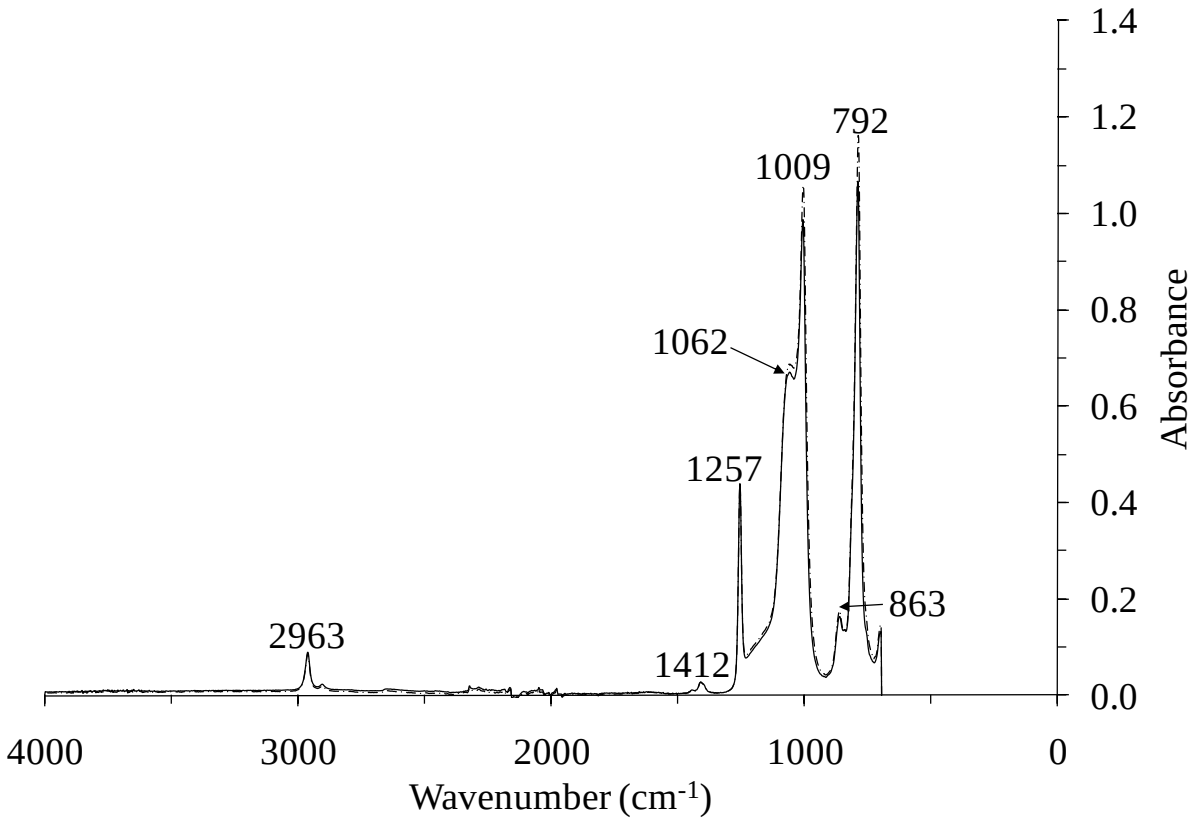

1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Absorbance
792
1009
1062
1257
863
2963
1412
4000
3000
2000
1000
0
Wavenumber (cm-1)

Fig. 4