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The effect of accelerated ageing on performance properties of addition type silicone biomaterials

K. Stathi · P. A. Tarantili · G. Polyzois

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Abstract The UV-protection provided to addition type silicone elastomers by various colorants, such as conventional dry earth pigments, as well as the so called "functional or reactive" pigments, was investigated. Moreover, the effect of a UV light absorber and a silica filler was also explored. Under the experimental parameters of this work, the exposure of silicone to UV radiation resulted in some changes of the IR absorbance, thermal decomposition after 400°C, T_g and tensile properties, whereas the storage modulus of samples was not affected. The obtained spectroscopic data, as well as the results of TGA and storage modulus, were interpreted by assuming that chain scission takes place during aging, whereas the improvement of tensile strength allows the hypothesis of a post-curing process, initiated by UV radiation. Therefore, the increase of T_g could partly be due to the above reason and, furthermore, to the contribution of a rearrangement of chain fragments within the free volume of the elastomeric material. Regarding the evaluation of various coloring agents used in this work, the obtained results show that dry pigments are more sensitive to accelerated ageing conditions in comparison with functional liquid pigments. Moreover, the hydrophobic character of silicone matrix is enhanced, with the addition of this type pigments because of the vinyl functional silanes groups present in their chemical structure. Finally, it should be noted that the incorporation of silica nanofiller did not seem to prevent the silicone elastomer from degradation upon UV irradiation, but showed a significant reinforcing effect.

1 Introduction

Maxillofacial prostheses play an important role in rehabilitation following ablative surgery, congenital deformity or trauma. Silicone biopolymers are today the material of choice for the fabrication of facial prostheses because of chemical inertness, strength, durability and ease of manipulation [1]. The longevity of a prosthesis is dependent on several factors, including the material from which it is constructed and behavioral factors of the wearer. Over the years there have been several studies on the longevity of facial prostheses and older ones report wearing time for 6–12 months [2–4]. A more recent study reported a mean life span of 14 months [5]. Despite this little improvement the life span of the prostheses still remains relatively short. Clinical experience has indicated the need for frequent replacement of facial prostheses because rapid discoloration in the service environment and/or degradation of the physical and dynamic properties of silicone biopolymers [6, 7]. Studies have reported that color fading and deterioration of feathered edges (tear) were the most common for replacement of prostheses [3–5]. Discoloration may be the result of intrinsic or extrinsic colorations secondary to environmental factors. It is a combined multifactorial phenomenon and some of the factors involved are intrinsic characteristics of the material, type of colorants, cleaning habits, use of cosmetics or adhesives and environmental staining (e.g. climate, fungal, body secretions) [8–12].

Coloration of a facial prosthesis is typically achieved through the use of various colorants, such as inorganic dry

K. Stathi · P. A. Tarantili (✉)
Polymer Technology Laboratory, School of Chemical Engineering, National Technical University of Athens,
Heroon Polytechniou 9, Zographou, 15780 Athens, Greece
e-mail: taran@chemeng.ntua.gr

G. Polyzois
Division of Removable Prosthodontics, Dental School,
University of Athens, Thivon 2, Goudi, 11527 Athens, Greece

earth pigments, artists's oil colors, opacifiers, liquid cosmetics, organic and ceramic pigments, dye-precipitated clays and the newly developed "functional or reactive" pigments [13–17]. Also, in addition to colorants, other additives, such as photoprotective agents [13], UV light absorbers [18, 19] or silica fillers as thixotropic agents can be incorporated into the silicone elastomer base. Colorants and the other additives may affect the color stability and physical properties, e.g. tensile strength of the silicone polymer.

The resistance of the silicone backbone to high temperature oxidation exceeds that of most organic molecules. Under the influence of temperature, an oxidizing deterioration of Si–C bonds can be observed simultaneously with depolymerization, which leads to shortening of the average length of the chains or to decrease in the network mesh size [20].

Furthermore, silicone rubbers are known to exhibit a high resistance to various kinds of irradiation. Since the energy required to break the Si–O bond is high, silicone-based rubbers are resistant to UV irradiation. However, the formation of intermolecular cross-links upon exposure to irradiation has been established for a long time and has stimulated further studies in the vulcanization of silicones [21].

It is well known, for instance, that PDMS tends to form cross-links when exposed to high-energy radiation and, moreover, gases such as hydrogen and methane are formed as a result of this radiation attack [22].

Regarding the effect of fillers on the ageing of polymers, no general trends can be found in the related literature. In some cases, a stabilizing effect of fillers against oxidation is evidenced, whereas in other cases fillers induce undesirable catalytic effects, as shown by TiO_2 upon UV exposure.

Gamma irradiation is known to increase the cross-links density. It has been reported that ZnO and carbon black fillers tend to increase the rate of cross-linking under X-rays irradiation through the formation of chemical links between filler particles and polymer chains [23].

A long term natural ageing study in different types of silicone elastomers was carried out by Oldfield and Symes [24]. The best performance was shown by an iron oxide pigmented, heat-vulcanized, dimethyl silicone rubber with reduction of less than 10% in tensile strength, 25% in elongation at break and increase in hardness up to 4% after 20 years exposure at Australian sites.

Lewicki et al. [25] studied the ageing behavior of montorillonite reinforced hydroxyl terminated PDMS using degradative thermal analysis. Their results indicate that significant chemical changes take place within the nanocomposite during ageing, i.e. acid catalyzed hydrolysis, chain backbiting and recombination reactions, re-structuring the polymer-filler network into a more thermodynamically stable form.

Taking into account the above described literature results, some formulations of an addition type silicon elastomer were prepared and studied in this work. The purpose of this investigation was to evaluate the protection and stability provided to the silicone elastomer by various types of colorants, such as conventional dry earth pigments, as well as the newly introduced in the market "functional or reactive" pigments. In addition, the effect of a UV stabilizer and a silica filler was also explored. In order to collect the necessary data and discuss possible mechanisms, various tests and measurements were made such as, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), tensile tests and, finally, color tests carried out in a colorimeter.

2 Experimental

2.1 Materials

Vinyl terminated silicone elastomer Silastic MDX4-4210 (Dow Chemicals) was the silicone rubber used in this work.

The following dry pigments and additives were investigated:

Yellow (P215), green (P227), brown (P217), blue (P216) supplied from Principality Medical Ltd., in concentration of 0.2% w/w. According to the supplier's specifications, the chemical composition of these pigments is ferric oxide powders.

Functional pigments supplied by Technovent limited, UK, and more specifically: yellow (FI-202), green (FI-232), brown (FI-217), blue (FI-203) in 2.5% w/w. The surface of pigment granules was modified by vinyl functional silanes to impart hydrophobicity and functionality.

Tinuvin 770 (Ciba), 0.5% w/w, a hindered amine light stabilizer for applications demanding particularly high light stability.

The reinforcing agent WACKER HDK H15 (Wacker Chemie AG), i.e. a hydrophobic fumed silica, formed by the chemical reaction of hydrophobic WACKER HDK with organosilanes.

2.2 Specimens preparation

The silicone rubber samples were prepared by adding first the appropriate amount of pigment and then the cross-linking agent according to manufacturer's instructions. The mixture was cast into moulds and cured at room temperature for 12 h, to form sheets of 2 mm thickness. Silica was dispersed into the elastomer matrix under mechanical stirring for 15 min.

2.3 Accelerated ageing process

Samples from the above sheets were exposed to accelerated ageing environment, using the appropriate weatherometer chamber, type QUV-Weathering Testers (Q-Panel, Lab Products).

The aging tests were run according to ASTM D 4587-01 and ASTM D 4329-99. Specimens were exposed to repeated cycles, including exposure to UV-radiation and damp heating. The UV-radiation was produced by employing a lamp type UVB-313. Water in the bottom of the test chamber was heated, filling the chamber with hot vapor and creating 100% humidity at 50°C. The specific set-up of the accelerated ageing procedure performed in this work was:

i. 8 h UV-radiation with a power of 0.76 W/(m^2 nm) at 60 ± 2.5°C, and
ii. 4 h water-condensate at 50 ± 2.5°C.

2.4 Scanning electron microscopy (SEM)

Scanning electron microscopy was performed for better investigation of the surface of the reference specimen, as well as of the samples after 875 h exposure to accelerated ageing. For the observation, a Quanta 200 equipment, FEI (Hillsboro, OR, USA) was used, working at environmental mode function.

2.5 Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

For spectroscopic measurements (Nicolet FTIR spectrometer, model Magna IR 750; DTGS detector; Nichrome source; beamsplitter; KBr), a total of 100 scans were applied with a resolution up to 4 cm^{-1}. Spectra were obtained at the attenuated total reflectance (ATR) mode using a standard ZnSe 45° flat plate Contact Sampler (12 reflections; Spectra-Tech, USA) on which samples of vulcanized silicone were placed. Spectroscopic data were treated using the standard software (OMNIC 3.1, Nicolet).

All spectra were smoothed using the "automatic smooth" function of the above software, which uses the Savitsky–Golay algorithm (5-point moving second-degree polynomial). After the above procedure, the baseline was corrected using the "automatic baseline correct" function.

2.6 Thermogravimetric analysis (TGA)

Thermogravimetric tests in PDMS were performed with a Mettler Toledo thermogravimetric analyzer (model TGA-SDTA 851E). The analysis was run with samples of 10 mg at a heating rate of 10°C/min, from 25 to 700°C, under nitrogen flow.

2.7 Dynamic mechanical analysis

Dynamic mechanical analysis experiments were performed in a Perkin Elmer Analyzer (Diamond DMA) in tension mode, over a temperature ranging from −150 to 50°C at 1°C/min and frequencies of 0.1, 0.2, 0.5, 1 and 2 Hz.

2.8 Tensile properties

Tensile tests were carried out according to ASTM D 412 specification in an Instron (model 4466) tensometer, equipped with a load cell of maximum capacity of 10 kN, operating at grip separation speed of 100 mm/min. All measurements were run at 25°C.

2.9 Color test

Color changes (ΔE) were examined with a microcolor tristimulus colorimeter (Micromatch plus, Sheen Instruments). This instrument is designated to determine color characteristics in the CIE LAB color system according to ASTM D 2244-68. The system is an approximately uniform color space using three parameters (L, a, b) to define color, where (L) measures the light–dark character, (a) the red–green balance, and (b) the yellow–blue balance. Color change can be calculated from the following equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a_L)^2 + (\Delta b_L)^2} \qquad (1)$$

3 Results and discussion

3.1 SEM

After the 875 h exposure to the accelerated ageing program, the smooth elastomer surface became rough with some irregularities due to small cracks, as can be seen in Fig. 1b.

3.2 ATR

FTIR-ATR measurements (Fig. 2) were run in order to provide evidence about the possible chemical interactions taking place during the accelerated ageing procedure. Spectra of the irradiated specimens were obtained and compared with those of the same specimens before exposure. The peaks recorded for Silastic MDX4-4210 are presented in Table 1. With respect to the absorption intensity a decrease of the size of peaks corresponding to aged silicone specimens was observed, in comparison with those of reference specimens, but no clear evidence for the formation of oxygen containing groups was recorded. The above changes could be attributed to an attack of the

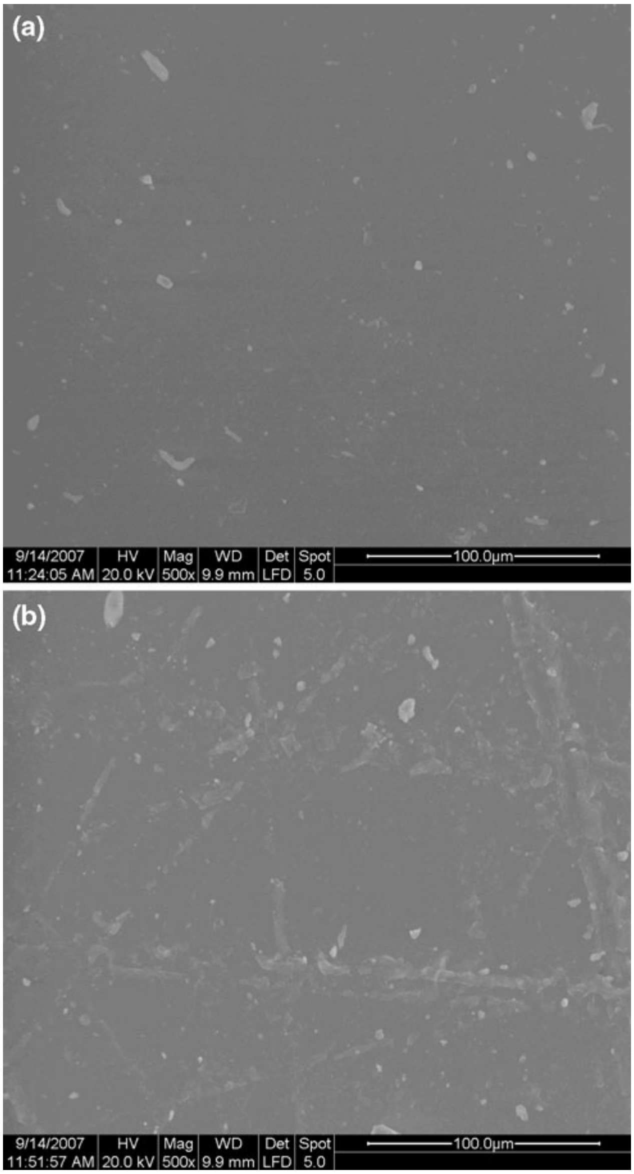

Fig. 1 SEM micrographs of **a** reference and **b** after 875 h exposure to accelerated ageing conditions specimens of Silastic MDX4-4210 (×500)

methyl side groups by action of UV radiation, or just to different surface arrangement of the specimens tested.

The photodecomposition of PDMS under UV irradiation has been studied by Delman et al. [26], who used IR spectroscopy. Their results indicate that $SiCH_2Si$ linkages were formed as a result of irradiation at wavelengths above 281 μm. On the other hand, Si–OH and $SiCH_2CH_2Si$ linkages were formed instead, when the resin was exposed to lower wavelengths.

The study of photodegradation of vinyl-PDMS by gas chromatography and mass spectroscopy, performed by Ysraeli et al. [27], revealed a very complex mixture of photoproducts as a result of chain scission and direct oxidation of the vinyl groups. According to the above work scission of the Si-vinyl bond seems to be the main degradation reaction.

No significant concentration of oxygenated products was detected in the IR spectra obtained by Virlogeux et al. [28], who tested high temperature vulcanized PDMS after 5,000 h of accelerated photo-ageing. However, an unexpected tendency to cross-link upon ageing was detected in the material, even in the absence of a peroxide cross-linker. The above authors interpreted this phenomenon by assuming chromophoric impurities or double bonds present in the industrial formulation, used in their work for specimens preparation.

The effect of environmental ageing on medical grade silicones was studied by Leslie et al. [29]. The changes in absorbances found by FTIR analysis between the reference and aged samples was attributed to competing processes, such as continued cross-linking alongside oxidation.

3.3 TGA

As shown in Fig. 3, TGA curves are almost the same for both types of specimens, for temperatures up to 400°C. However, within the range 400–700°C, the aged samples tend to lose weight more rapidly than the untreated silicone. This could be due to the already mentioned decrease of molecular weight of the aged silicone, because of chain scission promoted by UV radiation, or to other types of degradation taking place upon exposure to the high energy radiation.

3.4 DMA

Dynamic mechanical analysis was used to measure the viscoelastic properties of the silicone specimens exposed to accelerated ageing conditions, as a function of temperature. The thermal transitions were calculated from the obtained plots of $\tan\delta$. Silastic MDX4-4210 was found to display a glass transition at approximately −113°C and 1 Hz. At higher temperatures close to −35°C, a peak of different nature can also be observed, which would be associated with melting of the crystalline phase.

Figure 4 shows the curves derived from DMA analysis of Silastic samples. This analysis can provide an accurate assessment for glass transition temperature (T_g) of each sample and, moreover, it reveals the storage modulus. From the curves of Fig. 4 it is evident that the values of the above modulus versus temperature, remain the same for the as prepared and aged Silastic samples. Also, the incorporation of silica filler does not affect the moduli values, which is rather a result of its particle size. In fact, silica nanoparticles are probably too small to form additional cross-linking sites via surface interactions (polar or even

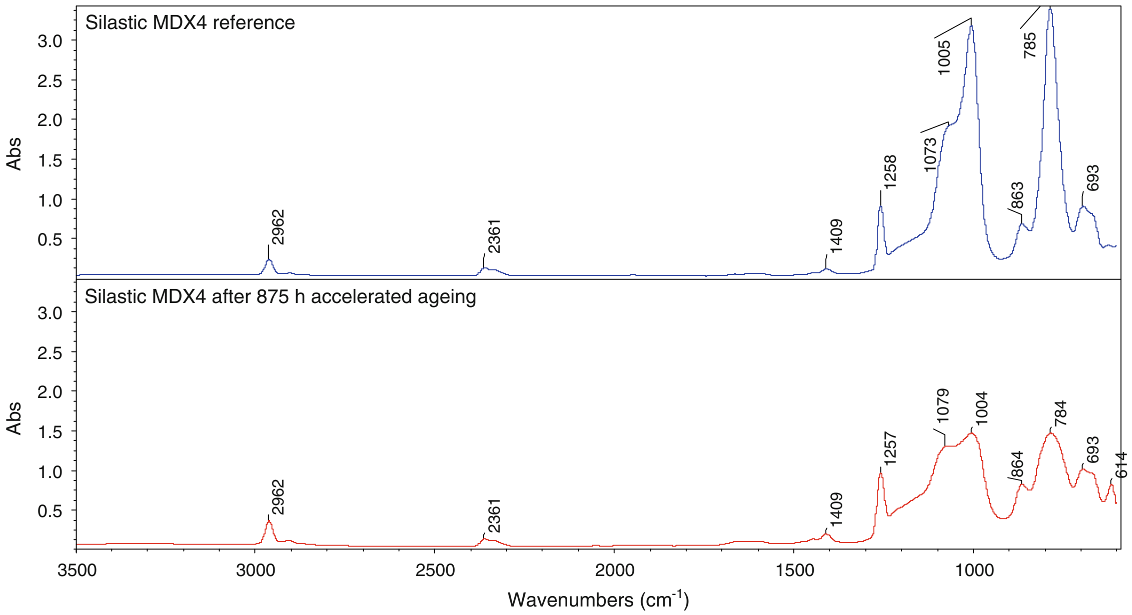

Fig. 2 ATR spectra of pigmented silicone elastomers specimens after exposure to accelerated ageing in comparison with unexposed (reference) specimens

Table 1 Assignment of IR spectra of Silastic MDX4-4210

IR region (cm^{-1})	Description
784	$-CH_3$ rocking and $\equiv Si-C\equiv$ stretching in $\equiv Si-CH_3$
825–865	$\equiv Si-O$ stretching in $\equiv Si-OH$
1,016	In-phase and out-of-phase vibrations of $-(CH_2)-$ in $\equiv Si-(CH_2)_2-Si\equiv$ and $\equiv Si-CH_2-Si\equiv$
1,258	Symmetric $-CH_3$ deformation in $\equiv Si-CH_3$
1,409	Asymmetric CH_3 deformation
2,962	Asymmetric $-CH_3$ deformation in $\equiv Si-CH_3$

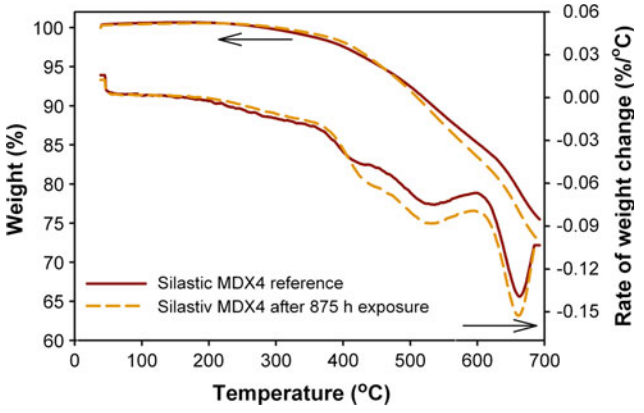

Fig. 3 Thermogravimetric analysis of silicone elastomers

chemical) with the silicone chains. This would contribute to an increase of cross-links and, further, to the increase of storage modulus of a certain sample. On the other hand,

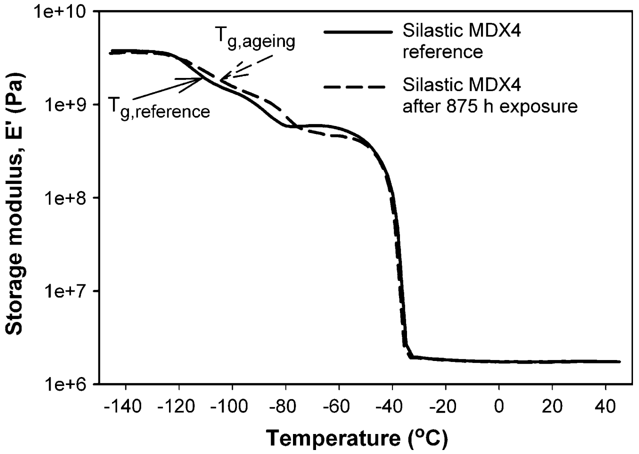

Fig. 4 Temperature dependence of storage (E′) modulus of Silastic MDX4-4210

Table 2 DMA data of Silastic MDX4-4210 derived from tanδ versus temperature graph at frequency of 1 Hz

Silastic MDX4-4210	T_g (°C)	T_m (°C)
Reference	−113.36	−34.87
After 875 h of accelerated ageing exposure	−108.84	−35.55

Table 2 shows an increase of the T_g of the aged samples. This suggests restricted mobility of the silicone backbone, a fact normally associated with increased cross-links density, but needs further evidence in order to be well established, since it derives from just one series of specimens. More specifically, the hypothesis of additional cross-linking reactions taking place upon irradiation cannot be supported by the results obtained so far from TGA experiments as well as from the storage modulus. In fact, these data rather suggest a break-down of the elastomers chains and, therefore, the increase of T_g could be at the time attributed rather to a rearrangement of the chain fragments within the free volume of specimens, after the scission reactions introduced by UV radiation.

Stevenson et al. [21] studied the irradiation ageing of silicone rubbers with and without filler using high resolution low frequency dynamic mechanical spectroscopy. Electron irradiation from 25 to 500 kGy have led to additional cross-linking and the apparent cross-links density was higher for filled elastomers due to additional links created in polymer-silica boundaries. They claimed that the amplitude of the glass transition mechanical relaxation appears to be correlated with the amplitude of the melting peak. The magnitude of the crystallization peak at −40°C decreases with the irradiation dose and this results in an increase of amplitude of the relaxation process associated with the glass transition near −125°C, since a larger amount of amorphous phase is present due to the hindrance of the crystallization behaviour.

It was reported that silicones with loadings of or in excess of 20 wt% fumed silica, exhibit a broad second thermal transition 40–50°C above glass transition, which extends for roughly 75°C. This thermal transition has been attributed to the polymer closely interacting with the silica filler, that was termed “bound polymer” [30].

3.5 Tensile tests

The mechanical characteristics of the original and aged specimens, in terms of tensile strength, modulus and strain at break, are shown in Table 3. From these results it is evident that mechanical properties of Silastic MDX4-4210 were improved after exposure to ageing conditions. Also, silica has a strong reinforcing effect on the examined silicone. On the other hand, the incorporation of silica nanoparticles into silicone samples does not essentially improve their resistance to ageing. The overall evaluation of the effect of ageing on tensile properties, shows that Silastic undergoes significant structure changes after the exposure program followed in this work. However, the increase in strength after 875 h ageing, which is accompanied by an increase of modulus, would indicate that some chain cross-linking occurred by exposure to UV-radiation. On the other hand, the observed increase of elongation could probably be due to molecular disentanglement taking place as a result of chain scission before their rearrangement via the formation of cross-links. The incorporation of silica particles does not contribute to this mechanism. Although the formation of bonding at the polymer-silica interface upon irradiation has been reported, in this case the incorporation of filler in combination with the increased temperature and moisture during ageing, rather promotes hydrolysis reactions and accelerated cleavage of siloxane backbone leading to the deterioration of tensile properties of the aged specimens in comparison with the original.

Chien et al. [31] studied the changes of cross-linking density and chemical structure of silica-reinforced silicone polymer composites due to the ageing caused by gamma radiation. Their results show that samples irradiated in air displayed an initial softening due to the loss of hydrogen bonding, normally taking place at the interface between the polymer matrix and the filler, whereas samples irradiated under vacuum presented higher stiffness upon irradiation, due to an increase of cross-links density in the polymer matrix and the formation of hydrogen bonding at the polymer/filler interface. Similar behaviour was reported by Maxwell et al. [32] for silica filled, room temperature vulcanized polysiloxane rubber exposed to gamma-irradiation.

Electron beam irradiation of peroxide cross-linked PDMS elastomer filled in air, with untreated and surface treated silica has led to additional cross-linking and the materials became more rigid and brittle. The apparent cross-linking density was higher for filled elastomers, since links at the polymer-silica interfaces have been created as a result of irradiation [21].

The chemical composition of pigmentation may also affect the mechanical properties of silicone elastomer. It was reported that iron oxide pigment, normally added to silicon rubber as a heat stabilizer, ensures better performance than that displayed by titanium oxide and carbon black pigmented elastomers [24].

Haug et al. [33] studied the effect of exposure to weathering and time on the physical properties of maxillofacial elastomers, such as medical adhesive type A,

Table 3 Tensile properties of Silastic MDX4-4210

Silastic MDX4-4210	Tensile strength (MPa)	Modulus of elasticity (MPa)	Strain at break (%)
Reference	2.03 ± 0.07	1.89 ± 0.09	241.05 ± 14.16
After 875 h of exposure	2.43 ± 0.11	1.95 ± 0.16	289.52 ± 19.68
+3% SiO_2 reference	3.25 ± 0.22	1.99 ± 0.10	298.00 ± 16.95
+3% SiO_2 after 875 h of exposure	2.76 ± 0.32	1.79 ± 0.04	253.24 ± 10.34

Silastic 4-4210 and Silicone A-2186. They found that the addition of colorants to elastomers enhanced the effect of weathering and the silicones were not as stable as previously determined.

3.6 Color measurements (Lab)

The color stability, in terms of the parameters determined by Lab chromatometry, for Silastic MDX4-4210 silicone elastomer is presented in Figs. 5, 6, 7, 8 and Table 4. A ΔE value of two units was considered the minimum significant color change that could be visually detected [34]. It is obvious that the unpigmented sample present minor color changes after exposure to accelerated ageing conditions. A color change ΔE of 5 was reported for unpigmented silicone type A-2186, stored in darkness for 45 days and this behaviour was explained as a result of additional cross-linking caused by continued polymerization of the elastomer or by side reactions among initiators, impurities present within the silicone, or by some other mechanism [33, 35]. Similar results were found for silicone samples colored with blue and brown dry pigments. The yellow and

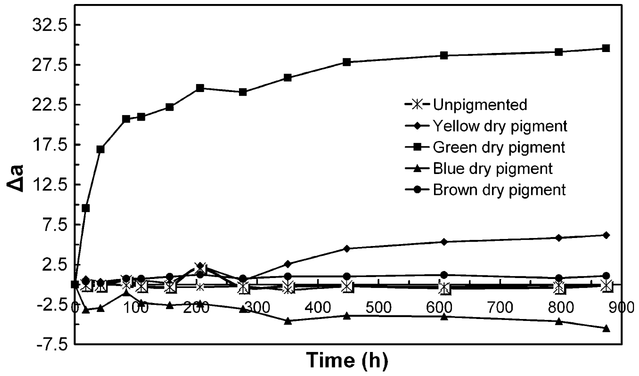

Fig. 5 The red–green character Δa as a function of time of during accelerated ageing of silicone elastomers colored with dry pigments

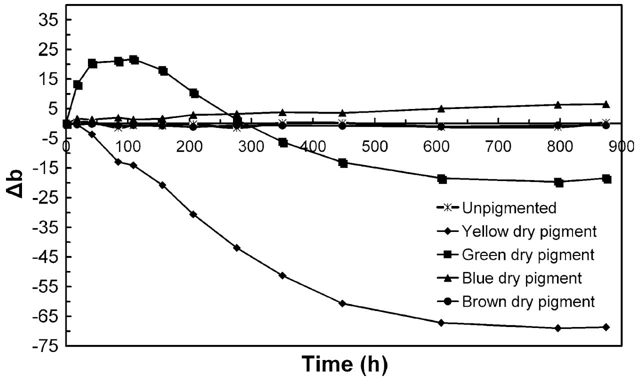

Fig. 6 The yellow–blue character Δb as a function of time of during accelerated ageing of silicone elastomers colored with dry pigments

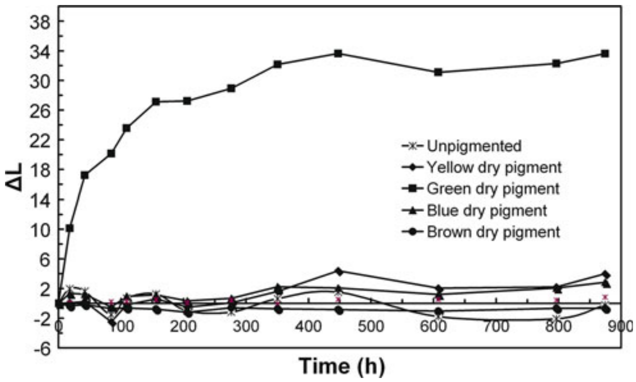

Fig. 7 The light–dark character ΔL as a function of time of during accelerated ageing of silicone elastomers colored with dry pigments

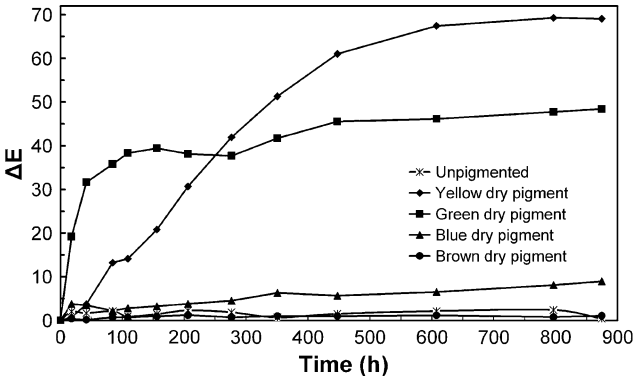

Fig. 8 The total color change ΔE as a function of time of during accelerated ageing of silicone elastomers colored with dry pigments

Table 4 Lab values of Silastic MDX4-4210 specimens after 875 h exposure to accelerated ageing conditions

Samples of Silastic MDX4	Δa	Δb	ΔL	ΔE
Unpigmented	−0.10	0.33	−0.21	0.41
Unpigmented + UV-stabilizer	−0.24	1.18	−0.90	2.25
+ Yellow dry pigment	6.18	−68.67	4.00	69.06
+ Yellow dry pigment + UV-stabilizer	7.79	−60.51	2.76	61.07
+ Yellow dry pigment + SiO_2	4.26	−59.48	−0.59	59.63
+ Green dry pigment	29.56	−18.43	33.63	48.42
+ Green dry pigment + UV-stabilizer	29.99	−21.37	32.61	49.19
+ Green dry pigment + SiO_2	29.75	−20.29	31.37	47.76
+ Blue dry pigment	−5.46	6.51	2.85	8.96
+ Blue dry pigment + UV-stabilizer	−0.95	5.54	2.28	6.06
+ Brown dry pigment	−0.11	−0.67	0.84	1.08
+ Brown dry pigment + UV-stabilizer	0.39	0.12	1.75	1.80
+ Yellow functional pigment	2.08	−8.86	−5.87	10.83
+ Green functional pigment	0.05	−0.15	0.04	0.16
+ Blue functional pigment	−4.12	6.42	2.70	8.09
+ Brown functional pigment	−0.56	−0.97	0.57	1.26

green colored samples underwent significant color change ($\Delta E > 2.0$) from the early stages of exposure. The color change of silicone colored with yellow pigment was attributed to the severe change of Δb component, which represents the chromaticity coordinate for yellow/blue. The change of green colored silicone was attributed to changes mainly in the component Δa and ΔL. From Fig. 8 it is obvious that the texture of green color changes during the first 50 h of exposure, whereas the change of yellow color is accomplished almost linearly during the first 500 h of ageing.

Some colorants tend to "protect" silicones from weathering, possibly by blocking light radiation and, thus, preventing it from acting within the entire elastomer mass [33]. It has also been reported that inorganic coloring agents are more stable to color changes in comparison with organic colorants [6].

Beatty et al. [35] evaluated the color changes in elastomers, pigmented with five dry pigments, after exposure to UVA and UVB light. Cosmetic red and cadmium yellow pigments underwent substantial color change after 400 h, whereas mars violet and cosmetic yellow ochre remained stable after 1,800 h. It is obvious that the chemical changes caused by compositional differences among various pigments may have produced the observed differences in color stability. However, pigment composition was generally unknown in the related studies as it remains proprietary information of the manufacturer.

The incorporation of fumed silica decreased the rate of yellow color change after the first 200 h of exposure. However, as can be seen in Table 4, no effect on the green color change of silicone samples was recorded with further incorporation of silica reinforcement.

Oil-based colorants used for pigmenting maxillofacial prostheses, demonstrated a wide range of vulnerability to UV radiation. It was postulated that either a chemical interaction or a chemical incompatibility between pigments and elastomer, permitting their migration during prolonged exposure to ultraviolet energy, can be responsible for the observed color changes [36].

A commonly observed clinical event is yellowing of the clear polyurethane backing film, which in part may be due to migration of yellow pigments present within the polydimethyl siloxane prosthesis. In addition, it must be taken into consideration that the surface chemistry of the oxide pigments is similar to untreated silica and, thus, capable to attracting moisture which may create color change. Therefore, a modification of pigment surface via vinyl functional silanes was proposed, in order to impart hydrophobicity and functionality. When incorporated into an active, vinyl terminated silicone elastomer, these functional pigments should ensure a fully chemically bound rubber matrix.

The functional pigments used in this work present very good color stability after 870 h of accelerated ageing exposure, as shown in Table 4. Among these types of pigments the more sensitive are yellow and blue colors as they display the higher ΔE values.

According to the experimental work of Takamata et al. [7] most of the color changes observed in HTV and RTV maxillofacial silicones were attributed to aging and not to exposure to sunlight.

UV-light exposure was the most significant factor causing discoloration in unpigmented and pigmented silicone samples compared with samples stored under dark controlled conditions, at elevated temperatures (35 and 50°C), as well as in saline solutions (0.15 and 5 M) for a period of 9 months [37].

Finally, it should be noted that Lemon et al. [18] studied the color stability of facial prostheses and found that artificial aging caused greater change than outdoor aging, which is reasonable taking into account the accelerated conditions of the former The above authors observed that the use of a UV light absorber as additive in the silicone elastomer did not protect the samples against color changes.

4 Conclusions

From the evaluation and discussion of the results obtained in this work we could draw the following conclusions:

Under the ageing conditions followed in the experimental set-up of this work, the exposure of addition type silicones to UV radiation showed an effect on IR absorbance, thermal decomposition after 400°C, T_g and tensile properties, whereas the storage modulus of samples remained rather constant. The spectroscopic data along with the results of TGA and storage modulus were interpreted by assuming chain scission of the aged polymer, whereas the improvement of tensile strength allows the hypothesis of further cross-linking initiated by UV radiation accompanied by possible chain disentanglement. Therefore, the increase of T_g could be due partly to the above reason assisted by a rearrangement of chain fragments within the free volume of the elastomeric material.

Regarding the evaluation of various coloring agents used in this work, the obtained results show that dry pigments are more sensitive to accelerating ageing conditions in comparison with functional liquid pigments. This can be explained by the increased stability achieved through the chemical interactions of liquid pigments with the silicone matrix. Moreover, the hydrophobic character of the silicone matrix is enhanced with the incorporation of this type pigments because of the vinyl functional silanes groups present in their chemical structure.

Finally, it should be noted that the addition of silica nanofiller did not prevent silicone elastomer from degradation upon UV irradiation, but showed a significant reinforcing effect.

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