J Mater Sci: Mater Med (2007) 18:1675–1681
DOI 10.1007/s10856-007-3027-4

Structural damages of maxillofacial biopolymers under solar aging

P. N. Eleni · M. K. Krokida · M. J. Frangou · G. L. Polyzois · Z. B. Maroulis · D. Marinos-Kouris

Received: 3 November 2005 / Accepted: 1 May 2006 / Published online: 5 May 2007
© Springer Science+Business Media, LLC 2007

Abstract Additional types of silicone biopolymers are widely used in maxillofacial prosthetics. Therefore, the knowledge of the solar radiation's effect on their structural stability is highly important. Four different industrially synthesized biomaterials were examined, called Episil Europe 1, Europe 2, Europe 3 and Africa 3, which were exposed to solar radiation (UVA, UVB) for eight different time periods (from 8 to 168 h). Structural damages due to irradiation exposure were investigated by mechanical tests (compression) and differential scanning calorimetry (DSC) methods. Simple mathematical models were developed, containing parameters with physical meaning such as maximum stress (σ_{max}), maximum strain (ε), elasticity parameter (E), and viscoelastic parameter (p), for the compression test, and melting temperature (T_m) and Enthalpy in melting point (*Heat*) for DSC. With increasing irradiation time their maximum stress and strain decreased significantly, and the materials lost their elasticity and molecular stability. A decrement in their melting points and heats was observed as irradiation time was increasing. Finally, experimental results demonstrated that solar radiation has a severe effect on the structural stability of the examined biomaterials.

P. N. Eleni (✉) · M. K. Krokida · Z. B. Maroulis · D. Marinos-Kouris
Department of Chemical Engineering, National Technical University of Athens, Zografou Campus, 15780 Athens, Greece
e-mail: peleni@central.ntua.gr

M. J. Frangou · G. L. Polyzois
Division of Removable Prosthodontics, University of Athens, Dental School, 2 Thivon Str., 11527 Athens, Greece

Introduction

Maxillofacial materials are used to replace missing facial parts which have been lost through disease or trauma [1]. The examined materials consist of siloxane. Silicone rubbers have in general the following advantageous characteristics: a wide service temperature range, non-adhesive properties, low toxicity, possible optical transparency, low chemical reactivity, and excellent resistance to attack by oxygen, ozone and sunlight [2]. Although they are widely used, these materials are far from ideal. Due to their exposure to several temperatures and forces, the knowledge of their thermal and mechanical properties as well as the effect of various factors on them are highly important. The quality of these materials depends greatly on their structural stability [3]. The most injurious factor for their structural stability, which also affects their mechanical and thermal properties, is solar radiation that causes disruption in polymers namely aging [4]. The effects of solar exposure are usually examined through differential scanning calorimetry (DSC), compression, and other thermal and mechanical methods [5, 6].

The effect of γ-radiation has already been examined on the thermal, mechanical, and segmental dynamics of polydimethyl-siloxane (PDMS), using thermal, mechanical, chemical, and segmental methods. Each of these analytical methods identifies different aspects of the degradation mechanism [2]. It has been proved that dental materials provide an increase in their hardness after accelerated aging [7]. Tensile properties of the irradiated polymer after accelerated aging reproduce successfully the behaviour of the naturally aged components. The effect of microwave on thermal and

mechanical properties of samples which are used as dental base materials has also been examined [8]. The microwaves represent an accelerated method of aging. It is widely known that, apart from accelerated aging, the thermal and mechanical properties of those materials are affected by many factors. One of them is preparation time cure that has been already examined [9, 10].

However, it is also widely recognised that self-storage for long periods of time after irradiation in air, i.e. longer than 5–6 years, causes material degradation. This occurs via an oxidation process, which is chemically reflected by the presence of carbonyl groups [4]. In contrast, there has been little work done regarding changes that may occur in filled siloxane copolymer systems subjected to high-energy radiation [2]. Numerous studies have also been made for the indagation of new elastomeric materials for facial prostheses [1].

Thermal analysis methods of polymer characterization relevant to processing are well established and require an understanding of thermal and chemical stability, phase transition temperatures and kinetics, rheology (melt or solution as appropriate) and molecular relaxation times [5]. Over the past decades, thermal analysis has emerged as the most commonly used technique for the characterization of polymers. Turi has summarized polymer thermal analysis in two volumes [11]. DSC, already applied in the past to the study of photo polymerisation [12–14], allows the direct determination of the rate of reaction, assuming that the heat produced by the polymerisation is proportional to the number of monomer units reacted. Until now no one has expounded a simple mathematical model to describe biomaterial behaviour following exposure to solar radiation.

The present study deals with the structural damages of biopolymers after accelerated aging (UVA, UVB radiation). The variation in their structural stability was examined through compression and thermal (differential scanning calorimetry) tests. Differential scanning calorimetry was used in order to measure their phase transition temperature and enthalpy, which were correlated with solar irradiation time. Compression tests were used in order to comprehend the effect of solar irradiation upon stress and strain. A number of mathematical models were examined, and the most suitable and simple were selected according to the experimental data [15], which involve parameters with physical meaning, such as maximum stress (σ_{max}), maximum strain (ε), elasticity parameter (E), and viscoelastic parameter (p). These parameters were also correlated with solar radiation time.

Materials and methods

Materials

The materials that were examined are an additional type silicone, with different colours named Episil Europe1, Europe 2, Europe 3, and Africa 3, manufactured by Dreve-Dentamid GmbH, Germany. Their basic structure unit is siloxane. These biopolymers are produced in bulk and then shaped for a specific end use. The difference of the four samples was the colour. The biomaterials were not used as received. The samples were placed in an oven for 2 h at 100 °C into matrices.

Irradiation

Polymeric materials that are used for external maxillofacial applications are subjected to attack typically by ultraviolet light, oxygen, and water. No single light exposure apparatus can exactly simulate natural exposure but it is a good approaximation.

The specimens from each colour were artificially aged in an irradiation machine and exposed in ultraviolet light. The test was run for a total radiant energy of 1.35 W/m^2, and the total exposure time of 168 h (eight different time periods—8, 24, 48, 72, 96, 120, 144 and finally 168 h). The test was conducted according to ASTM D4329-99—Standard Practice for Fluorescent UV Exposure of Plastics [16]. Ultraviolet radiation induced radical formation mechanisms, which involve either permanent chain scission or radical recombination to form structural irregularities in the specimens' chains.

Compression test

From each material (colour) two hardness specimens were made for each irradiation time. The hardness test was conducted according to ASTM D 695, ISO 604—Standard Test Method for Compressive Properties of Rigid Plastics using a (Universal Testing Machine) Zwick model 3210 [17]. The uniaxial compression tests were performed at room temperature (25 °C). Two TA—25 probes (10 cm diameter cylinder) were fitted to the instrument. Force and deformation were recorded electronically and the resulting stress–strain compression curves were constructed.

Thermal test

Differential scanning calorimetry

Differential scanning calorimetry analyses were performed by heating the samples at a rate of 10 °C/min from 20 °C to

350 °C. This method uses individual heaters to maintain identical temperatures for two small platinum holders, one containing the small (25–27 mg) sample mechanically sealed in a small aluminium pan, and the other containing an empty (reference) pan. The DSC test was conducted according to ASTM E794:01—Standard Test Method for Melting and Crystallization Temperatures, using a (differential scanning calorimeter) Perkin Elmer model Pyris 6 [18]. Heat-Temperature curves were recorded electronically.

Mathematical modelling

Several mathematical models were used in order to predict the value of stress, strain, elasticity, and viscoelastic parameters according to irradiation time for the compression tests, and temperature and enthalpy at the melting point, for the differential scanning calorimetry tests.

The most simple and appropriate model has been selected and summarised on Table 1 for the compression tests. The stress–strain equation (Eq. 1) that describes the viscoelastic behaviour [15] involves four parameters: the maximum stress (σ_{max}), the corresponding strain (e_{max}), the elasticity parameter (E), and the viscoelastic exponent (p). Maximum stress and strain represent the break point of the compression test. The elasticity parameter represents the linear part of the stress–strain curve and shows the elastic nature of the material. The viscoelastic exponent represents the exponential part of the curve. Irradiation affected all the above parameters. Thus, they correlated with irradiation time. In particular, maximum stress, corresponding strain, and elasticity parameter were found to decrease, as the irradiation time was increased, contrary to the viscoelastic exponent behavior which is the opposite. This experimental behaviour is well defined by the following equations.

$$\sigma = \mathrm{E} * \varepsilon + (\sigma_{max} - \mathrm{E} * \varepsilon_{max}) * (\varepsilon/\varepsilon_{max})^{p} \quad (1)$$

where σ_{max} is the maximum stress, ε_{max} the maximum strain, E the elasticity parameter, p the viscoelastic exponent, σ and ε are the experimental data.

$$\sigma_{max} = \sigma_0 * (t_{ir}/85)^{k_1} \quad (2)$$

where σ_0, k_1 are constants and t_{ir} the irradiation time.

$$\varepsilon_{max} = \varepsilon_0 * (t_{ir}/85)^{k_2} \quad (3)$$

where ε_0, k_2 are constants and t_{ir} the irradiation time.

The values of E and p were correlated to the irradiation time through the following exponential relations.

$$E = E_0 * (t_{ir}/85)^{k_3} \quad (4)$$

$$p = p_0 * (t_{ir}/85)^{k_4} \quad (5)$$

where E_0, p_0, k_3, k_4 are constants.

A second mathematical model was selected and used to predict temperature and enthalpy curves for the differential scanning calorimetry (DSC) tests and is summarized on Table 2. The temperature and enthalpy at the melting point seemed to decrease as the irradiation time was increasing. The following equations depict well their behaviour.

$$T_{mp} = T_0 * (t_{ir}/85)^{n} \quad (6)$$

$$Heat = H_0 * (t_{ir}/85)^{m} \quad (7)$$

where T_0, H_0, n, m are constants

Table 1 Mathematical model for compression tests

Compression test		
Viscoelastic behavior (Stress–strain equation)		
$\sigma = \mathrm{E} * \varepsilon + (\sigma_{max} - \mathrm{E} * \varepsilon_{max}) * (\varepsilon/\varepsilon_{max})^{p}$		
Parameters		
σ_{max}	maximum stress	(kPa)
ε	maximum strain	(mm/mm)
E	elasticity parameter	(kPa)
p	viscoelastic parameter	(–)
Parameter equations		
$\sigma_{max} = \sigma_0 * (t_{ir}/t_0)^{k_1}$		
$\varepsilon_{max} = \varepsilon_0 * (t_{ir}/t_0)^{k_2}$		
$E = E_0 * (t_{ir}/t_0)^{k_3}$		
$p = p_0 * (t_{ir}/t_0)^{k_4}$		
Where		
σ	stress	(kPa)
ε	strain	(mm/mm)
t_{ir}	irradiation time	(h)
t_0	reference time	(h)

Results and discussion

Maxillofacial prostheses play a critical role in the rehabilitation of patients who have severe facial disfigurement.

Table 2 Mathematical model for DSC tests

Differential scanning calorimetry test		
Parameter equations		
$T_{mp} = T_0 * (t_{ir}/t_0)^{n}$		
$Heat = H_0 * (t_{ir}/t_0)^{m}$		
Where		
T	Temperature in melting point	(°C)
$Heat$	Enthalpy in melting point	(mW)
t_{ir}	irradiation time	(h)
T_0	reference time	(h)

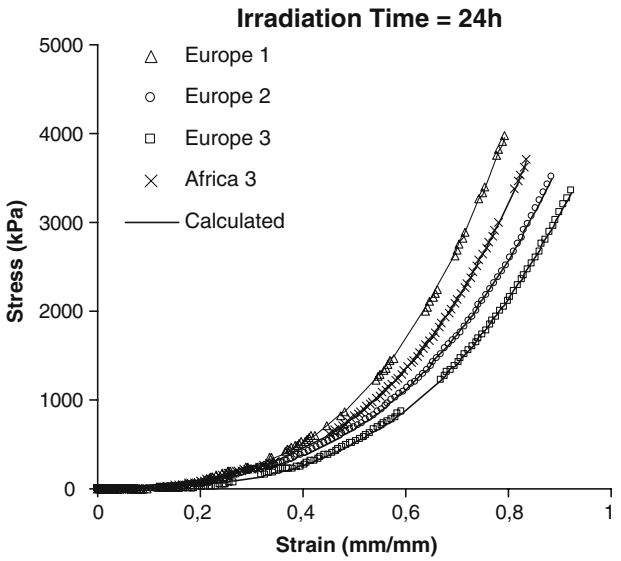


Fig. 1 Stress–strain curves of 24 h irradiated samples of all the colours (episil Europe 1, episil Europe 2, episil Europe 3, episil Africa 3)

The materials ought to mimic the natural behaviour of facial skin; as a result, they must be thoroughly examined, so knowledge of the most injurious factors among them and the manner in which they degrade them are highly important.

Typical stress–strain curves obtained from compression tests on materials irradiated for the same time period from the four different colours, (Episil Europe 1, Episil Europe 2, Episil Europe 3 and Episil Africa 3) are presented in Fig. 1. The stress–strain curves indicate that the colour of the specimens does not significantly affect their mechanical behaviour under solar exposure.

The affect of UV radiation on the structural stability and the mechanical behaviour of them are presented in Fig. 2 and, as indicated in them, the irradiation time has a significant influence on the stress–strain curves, for all the colours.

The calculated stress–strain curves resulted from the stress–strain equation, which contains maximum stress and maximum strain as parameters. Their values were calculated using Eqs. 2 and 3, for various time periods of irradiation and for each colour. Maximum stress and strain are related to the durability of the materials.

The results of parameter estimation of the mathematical model for maximum stress and strain (Eqs. 2 and 3) that was used are summarised on Table 3. The model was fitted to the experimental data, which were received from the

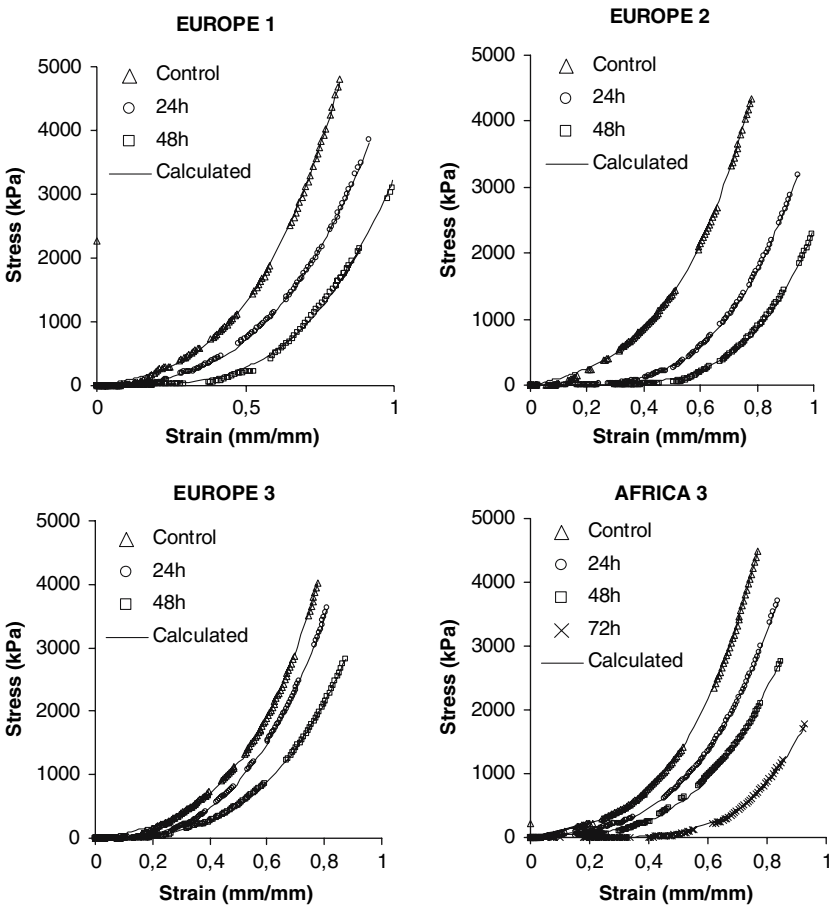


Fig. 2 Stress and strain curves for different time of irradiated Europe 1, Europe 2, Europe 3 and Africa 3 samples

Table 3 Parameter estimation for maximum stress maximum strain

Type of material	σ_0 (kPa)	k_1	ε_0 (mm/mm)	k_2
Europe 1	1690.18	–0.05	0.58	–0.04
Europe 2	975.34	–0.06	0.41	–0.04
Europe 3	601.69	–0.10	0.34	–0.04
Africa 3	2511.43	–0.04	0.76	–0.02

stress–strain curves. The correlation of maximum stress and maximum strain with irradiation time is presented in Fig. 3. The maximum stress and strain are presenting a decrement while irradiation time was increasing, for all the colours. The samples' colour and how this affects the decrement of maximum stress and strain is also reported in Fig. 3. The higher stress and strain values were denoted for samples Episil Africa 3, and the lower ones for samples Episil Europe 3.

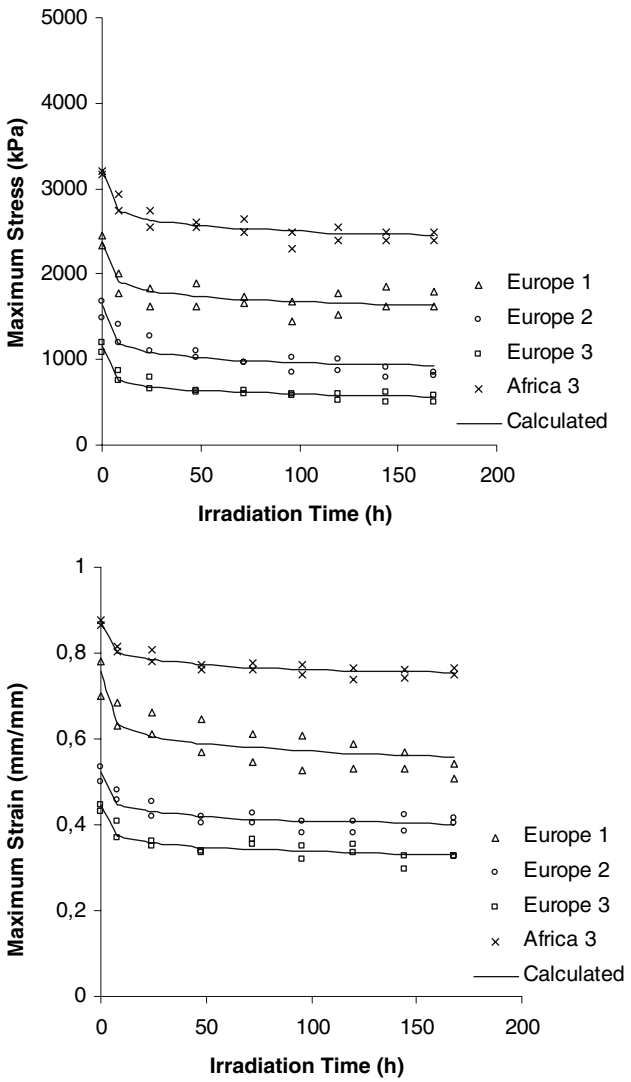


Fig. 3 Maximum stress and maximum strain for samples of the four colours

In the proposed model for maximum stress and strain, there were two other parameters, the elasticity parameter E, which gives the slope of the elastic part, and the viscoelastic exponent, p. Both of these parameters depend on the irradiation time. The results of parameter estimation for the elasticity parameter E and the viscoelastic parameter are summarised on Table 4.

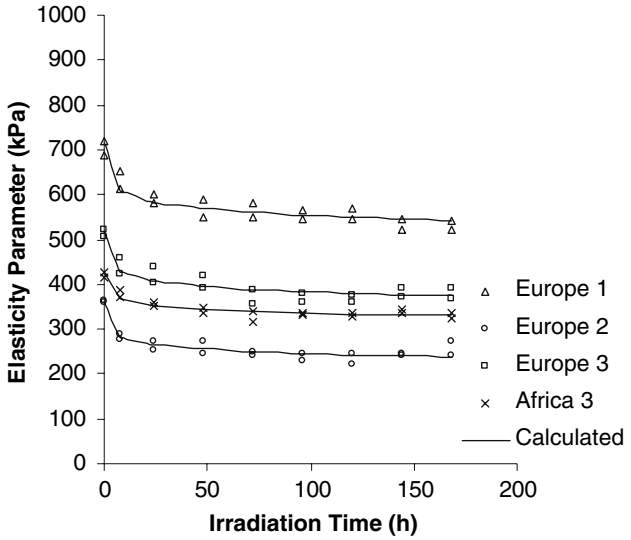
The elasticity parameter was found to decrease whith irradiation time. The viscoelastic parameter expresses the deviation from linearity and was also found to increase with irradiation time (Fig. 4). Specimens from all the colours had the same behaviour. The higher elasticity values were denoted for samples of Episil Europe 1 and the lower for samples of Episil Europe 2. As for the parameter p of the model, the higher values were noted for samples of Episil Africa 3 and the lower ones for samples of Episil Europe 3.

Figures 1 and 2 are indicatives of the mechanical degradation caused by the irradiation of all the samples in all irradiation times. The experimental data shown, are an average of three replications. The standard deviation in Figures 3 and 4 calculated in order to exhibit the experimental repeatability and is 5%. This rate is in the range of acceptable experimental faults and thereby it is safe to export conclusions.

Differential scanning calorimetry can be used to measure a number of characteristic parameters of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures (T_g). These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity, but no formal phase change occurs. As the temperature increases, an amorphous solid will become less viscous. At some point the molecules will obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (T_c). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature (T_m). The melting process results in an endothermic peak in the DSC curve. In Figs. 5 and 6 it is observed a crystallization exotherm prior to the melting endotherm.

Table 4 Parameter estimation of compression model

Type of material	E_0 (kPa)	k_3	p_0	k_4
Europe 1	556.12	–0.04	4.05	0.020
Europe 2	247.11	–0.06	3.60	0.026
Europe 3	385.75	–0.04	3.30	0.027
Africa 3	337.92	–0.03	4.16	0.017



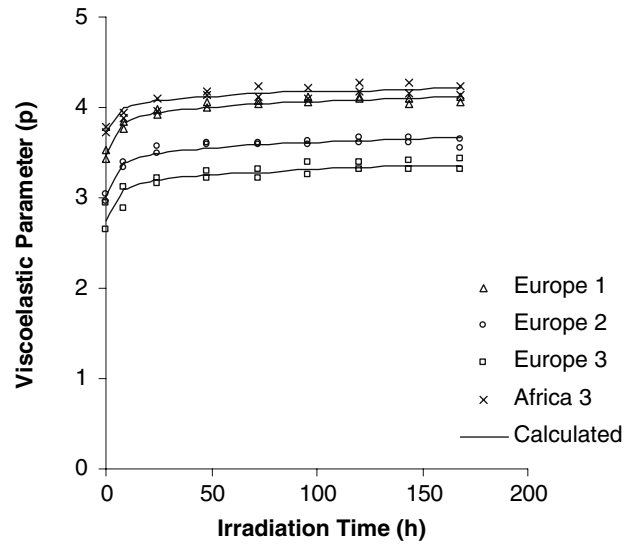


Fig. 4 Elasticity parameter and viscoelastic exponent for different time of irradiated samples of the four colours

A typical Heat–Temperature curve obtained from differential scanning calorimetry tests on materials is presented in Fig. 5.

The calculated melting points and enthalpy curves resulted from the model for the DSC tests (Eqs. 6 and 7) that contains maximum temperature (T_{mp}) and Enthalpy (Heat) as parameters. The values of these parameters for different time periods of irradiation and for each colour came out from Eqs. 6 and 7.

The results of parameter estimation of the mathematical model for maximum temperature (T_{mp}) and Enthalpy (Eqs. 6 and 7) that was used are summarised on Table 5. The model was fitted to the experimental data, which were received from the Enthalpy–Temperature curves. Enthalpy–Temperature curves for each colour that were irradiated for the same time period (24 h) are represented

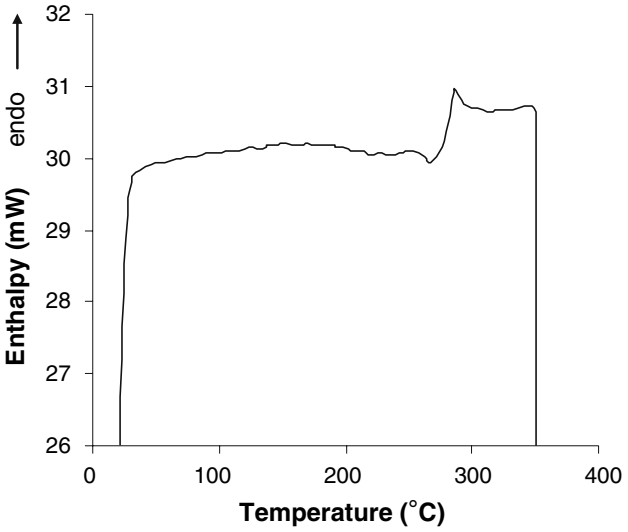


Fig. 5 Typical Enthalpy–Temperature curve of differential scanning calorimetry tests

Table 5 Parameter estimation for melting temperature and enthalpy

Type of material	T_0(°C)	n	H_0 (mW)	m
Europe 1	258.76	–0.010	28.52	–0.003
Europe 2	242.05	–0.014	26.83	–0.005
Europe 3	274.56	–0.011	27.54	–0.004
Africa 3	263.63	–0.011	28.69	–0.004

in Fig. 6. It is obvious that the colour of the materials influence their behaviour. The correlation of maximum Temperature (T_{mp}) and Enthalpy with irradiation time is presented in Fig. 7. The decrement of (T_{mp}) and Heat is obvious while the irradiation time was increasing for the

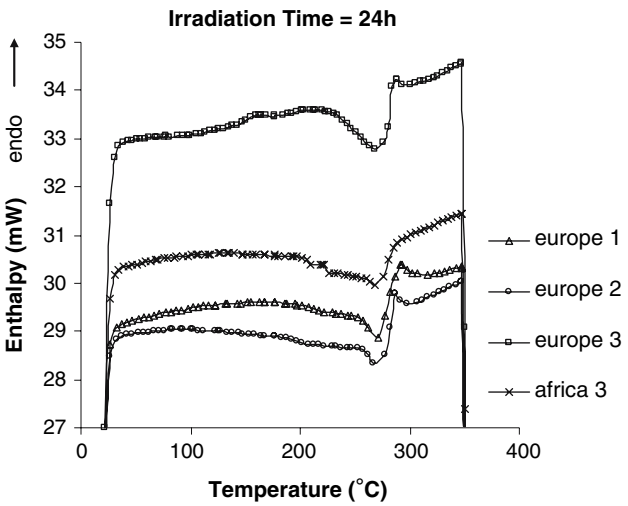


Fig. 6 Enthalpy–Temperature curve of differential scanning calorimetry tests of 24 hours irradiated samples of all the colours (episil Europe 1, episil Europe 2, episil Europe 3, episil Africa 3)

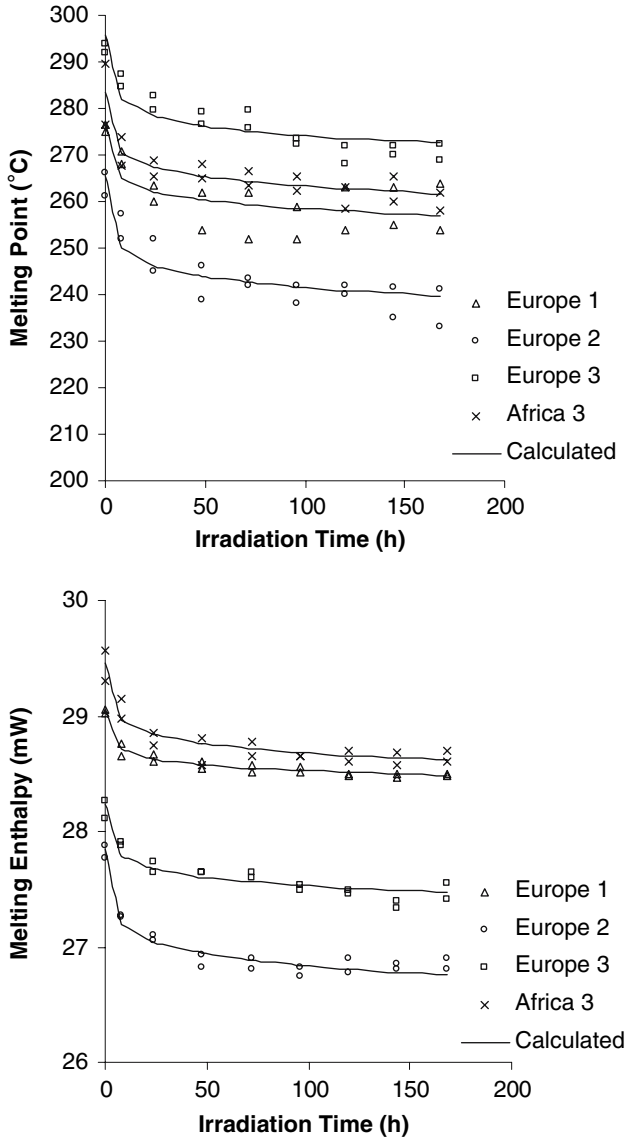


Fig. 7 Temperature and enthalpy at melting point for samples of the four colours

specimens of all the colours. The effect of the colour in the two parameters' values is also presented in Fig. 7. The higher melting temperature values were denoted for Episil Europe 3 and the lower for Episil Europe 2 samples; as for Heat, the higher values were denoted for Episil Africa 3 and the lower for Episil Europe 2 samples.

Conclusion

Silicone rubber materials used in maxillofacial prostheses have been examined following accelerated aging under UV radiation, simulating solar aging. Simple compression and thermal tests were performed. The results show significant differences observed in the mechanical and thermal behaviour between the control (unirradiated samples) and irradiated samples as a result of the degradation caused by the UV radiation. The main structural modifications seen in irradiated polymers are changes in molecular weight distribution -due to main-chain scission, cross linking and end linking- and the production of volatile degradation products [2, 19, 20]. The abiding exposition to solar radiation of these materials affects the compression behaviour that was investigated through the effect on the four parameters of the mathematical model which was used. It seems to incur a decrement in their maximum stress (σ_{max}), strain (ε_{max}) and elasticity parameter (E), and an increment in the viscoelastic exponent (p) while they were loosing their elasticity and molecular stability. In addition, there was observed a decrement in their melting points and heats. Finally the colour of materials that was examined had no significant effect upon their behavior to solar exposure.

References

1. K. BELLAMY, G. LIMBERT, M. G. WATERS and J. MIDDLETON, *Biomaterials* **24** (2003) 5061
2. R. S. MAXWELL, R. COHENOUR, W. SUNG, D. SOLYOM and M. PATEL, *Polym. Degrad. Stab.* **80** (2003) 443
3. M. BRADEN, *Biomaterials* **13** (1992) 333
4. F. MEDEL, E. G. BARRENA, F. G. ALVAREZ, R. RIOS, L. G. VILLA and J. A. PUERTOLAS, *Biomaterials* **25** (2004) 9
5. M. JAFFE, Z. OPHIR and V. PAI, *Therm. Acta*. **396** (2003) 141
6. I. SIDERIDOU, D. S. ACHILIAS and E. KYRIKOU, *Biomaterials* **25** (2004) 3087
7. K. A. SCHULZE, S. J. MARSHALL, S. A. GANSKY and G. W. MARSHALL, *Dent. Mater*. **19** (2003) 612
8. A. USANMAZ, J. ATES and A. DOGAN, *J. Appl. Polym. Sci*. **90** (2003) 251
9. A. USANMAZ, F. TURKER, A. DOGAN and N. AKKAS, *J. Appl. Polym. Sc*. **69** (1998) 1409
10. A. MAFFEZZOLI and R. TERZI, *Therm. Acta*. **269/270** (1995) 319
11. A. TURI, *Polymer Test*. **16** (1997) 523
12. W. D. COOK, *Polymer*. **33** (1992) 600
13. J. G. KLOOSTERBOER and G. F. C. M. LIJTEN, *Polymer*. **28** (1987) 1149
14. J. VAIDYANATHAN, T. K. VAIDYANATHAN, Y. WANG and T. VISWANADHAN, *J. Oral Rehabil*. **19** (1992) 49
15. M. K. KROKIDA, V. T. KARATHANOS and Z. B. MAROULIS, *Drying Technol*. **18** (2000) 395
16. ASTM D4329 Standard Practice for Fluorescent UV Exposure of Plastics Volume. American Society for Testing Materials. 2000; 08.03: 325
17. ASTM D695. Standard Test Method for Compressive Properties of Rigid Plastics. American Society for Testing Materials. 1993; 08.01: 145
18. ASTM E794. Standard Test Method for Melting and Crystallization Temperatures. American Society for Testing Materials. 2001: 14.02: 437
19. E. R. DOOTZ, A. KORAN and R. G. CRAIG, *J. Prosthet. Dent*. **69** (1993) 114
20. J. H. GUO, *Pharm. Sci. Technol. Today*. **18** (1999) 395