Solid State Characterization of Commercially Available Silicone Polymers Used in Maxilofacial Prostheses

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This paper reports the results obtained after completing the solid-state characterization of two commercially-available silicone polymer samples used in maxillofacial prostheses. The samples were prepared by the same technique, one being freshly prepared, while other having approximately 11 years. As investigational tools, FTIR spectroscopy was used, thermal analysis in air atmosphere and later a preliminary kinetic parameters evaluation by using the Coats-Redfern method.

Keywords: medical silicone, maxillofacial prostheses, thermal analysis, kinetic study, Coats-Redfern

Polymers are nowadays widespread in numerous scientific, technical and every-day use fields. Several types of polymers are nowadays used in medicine and related domains, like plastination and preparation of corrosion casts [1-6] or even as embedding materials for easing the sample preparation of biliary stones [7].

Prosthetic materials used in maxillofacial domain are mainly used as substitute to different facial parts lost by trauma or removed due to different pathologies. Since loss of body parts can affect human beings by decreasing the self-esteem, several methods and materials were investigated over the years in order to obtain similar structures and protocols that can replace the lost body parts, at least visual if not completely functional.

In the maxillofacial domain, elastomeric silicone rubbers are one the most used materials [8,9].

The paper of Bugum *et al.* investigated the properties of commercially available silicone Cosmesil-type elastomers for maxillofacial prostheses, including tensile strength, tear strength, hardness and water absorption [10], but no data regarding the comparative thermal and spectroscopic properties between freshly-prepared samples *vs.* old ones were found in literature.

Thermal analysis and kinetic study are of greatly importance nowadays in medico-pharmaceutical field, since it is a fast and easy-reproducible tool in characterization of materials, that was extensively used in the UMFVB research group [11-23]. Thermal analysis is used especially in evaluating the stability of samples during heating, and corroboration with other techniques, like evolved gas analysis and kinetic study can reveal important information over decomposition mechanism and interactions between components in mixtures. Mathematical models for kinetic analysis of solid-state non-homogenous decomposition are divided into two categories, depending on the way that the thermal data are processed. Initially, model-fitting protocols were developed and later model-free protocols were introduced, while the measurements were carried out in isothermal or non-isothermal conditions. The main advantages of model-free kinetics were elsewhere reported [14, 20-24], but a study using model-fitting methods can be used as a preliminary study.

Following the above-mentioned considerations, the aim of this paper was to report comparatively the solid-state properties of two commercially-available silicone polymer samples used in maxillofacial prostheses (Cosmesil Platinum Series) – a freshly prepared one (2 weaks older) *vs.* an old sample (11 years). As investigational tools, FTIR spectroscopy was used, followed by thermal analysis and completed with a preliminary estimation of kinetic parameters (E_a-activation energy and A- pre-exponential factor) using the Coats-Redfern method.

Experimental part

Material and methods

Cosmesil Platinum ® Series Standard Base (Product code P001) was commercial product of Principality Medical Limited (Western Valley Road, Rogerstone, Newport, South Wales, UK). The product consists in a dispersion of fumed silica particles in fluid silicone.

The hardening of the silicone is achieved by mixing it with a catalyst, supplied by the same producer. The mixing ratio was 10:1 m/m (Standard base: Catalyst). After mixing of components, the curing was realised under ambient conditions for approximately 24 h. Two samples were analysed (SIL1 – freshly prepared, and SIL2 – 11 years old).

The FTIR spectra of silicone samples (SIL1 and SIL2) were built using a Perkin Elmer SPECTRUM 100 device without preliminary preparation of the sample, directly on the UATR device. The reason for choosing UATR technique is due to the impossibility of KBr dispersion preparation due to the structure of polymeric films. Spectroscopic data were collected in the range 4000-600 cm^{-1} wavenumber domain and spectra were built up after a number of 16 acquisitions, at a resolution of 4 cm^{-1}.

Thermoanalytical curves (TG/DTG/DSC) was recorded using a NETZSCH STA 449C thermobalance. Samples were heated in alumina crucible in dynamic air atmosphere with a flow of 20 $mL \cdot min^{-1}$, with a heating rate $\beta = 10\ K \cdot min^{-1}$.

Results and discussions

The ATR-FTIR spectra of SIL1 and SIL2 samples reveal a very similar profile. Silicones, siloxanes and poly (dimethylsiloxane) show strong absorption bands in the

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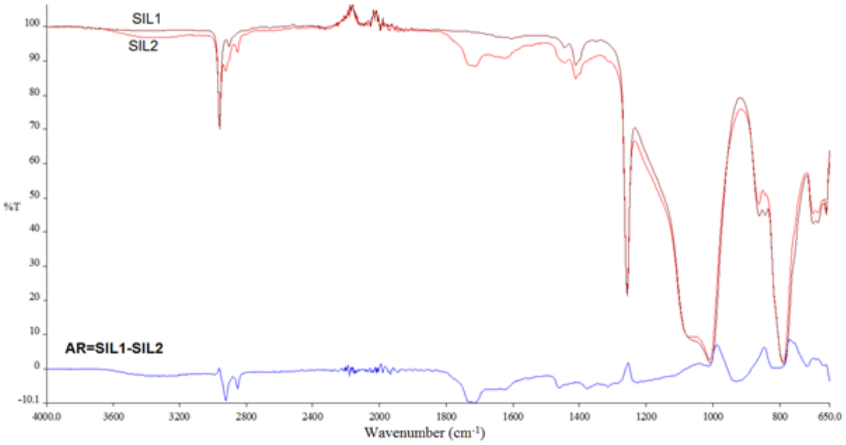


Fig. 1. ATR-FTIR spectra of SIL1 and SIL2 samples, in comparison with the arithmetic subtraction of SIL2 spectra from SIL1

mid-infrared spectrum range, at 1259, 1034 and 789cm^{-1}. The ATR-FTIR spectrum of SIL1 sample presents some bands, as follows: Si-C vibrations show a very strong absorption maximum at 1259 cm^{-1} due to symmetric CH$_3$ deformation from Si-CH$_3$ group. Also, an intense band appears at 789 cm^{-1} due to Si-CH$_3$ stretching. Si-O stretching vibrations from Si-O-Si and Si-O-C bonds are generally placed in the 1090-1020cm^{-1} spectral range, in the recorded spectra the peak was noticed at 1034 cm^{-1}, with a shoulder at 1065cm^{-1}. The sharp medium bands appearing at 2963 and 2905 cm^{-1} are due to C-H stretching vibrations from methyl groups, grafted on the siloxane chain. Other bands appearing in the fingerprint region are due to skeletal deformation of the chain.

In comparison, the ATR-FTIR spectra of SIL2 sample show an approximately identical pattern, with some differences. Si-C vibrations appear at 1258 cm^{-1} while the Si-CH$_3$ stretching appears at 792 cm^{-1}. Si-O stretching vibrations from Si-O-Si and Si-O-C bonds are appear at 1037 cm^{-1}, with a shoulder at 1065cm^{-1}. The sharp medium bands appearing at 2962 cm^{-1}, 2926 cm^{-1} and 2855 cm^{-1} are due to C-H stretching vibrations from methyl groups, with some differences in comparison with SIL1 sample. Another band appears at 1722cm^{-1}, suggesting that a modification over long-time storage occurs. In order to have a clear view over modification of ATR-FTIR pattern over storage, the arithmetic difference between the spectra is presented in figure 1, in comparison to spectra of SIL1 and SIL2 samples (fig. 1). Since the modifications were observed for the methyl groups grafted on the siloxane chain, it is supposed that the degradation/modification occur at these groups, and not on the polysiloxanic chain.

Since ATR-FTIR spectroscopy indicate some modification over structure of samples during aging, a second technique (thermal analysis) was employed for a comparatively analysis of the two silicones.

In figures 2-4, mass curves, mass derivative and thermal profile is presented, comparatively for the two samples.

Mass curve (fig. 2) show a good thermal stability of the samples, due to the long-chained siloxane. SIL1 show no mass modification up to 123°C, when a decomposition process starts with a mass loss of 9.5% up to 411°C. The next mass loss process occurs in the 411-627°C temperature range, for this process the mass loss is 48.5%. at temperatures higher than 627 °C, mass remains constant due to the formation of inert inorganic compounds of silicon, most probably silica (residual mass 42%). For SIL2 sample, thermal stability and TG profile is different than in the previous case. SIL2 is stable up to 120°C, when a process with mass loss begins up to 464°C (Δm=41.7%), then continuing with another process, up to 570°C (Δm=24%). The thermal treatment at temperatures higher then 570 °C does not modify the mass (residual mass 34.3%). The separation of these processes is not well defined on the mass curve, but on the mass derivative curve, as shown in figure 3.

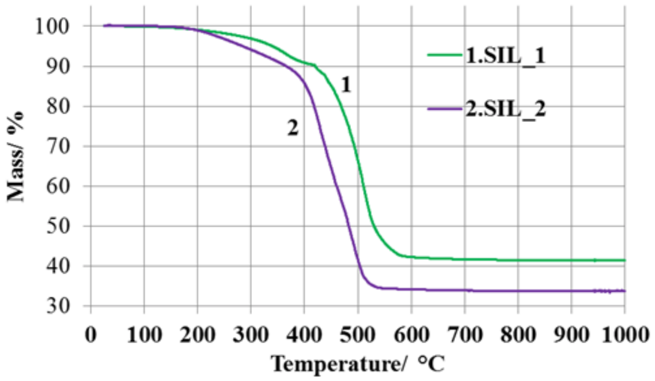


Fig. 2. Mass vs. temperature curves for the SIL1 and SIL2 samples

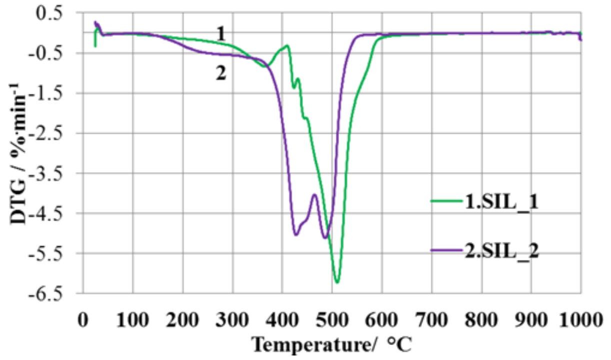


Fig. 3. Mass derivative vs. temperature curves for the SIL1 and SIL2 samples

The mass derivative curves (DTG) profile is different in the case of the two analysed samples. SIL1 show two main decomposition processes, the first having the onset temperature at 231°C, with a maximum at 365°C, while the second begins at 408°C, with a maximum at 512°C. For SIL2 sample, the main process has an onset temperature of 341°C with a peak at 425°C, while the second process is not very well separable, starting at 464 °C and a maximum at 484 °C.

The DSC profiles (fig. 4) is even more complex, consisting in overlapping of endothermic and exothermic effect (exo up). For SIL1 sample, the DSC onset occurs at 294 °C with a maximum at 36 °C (exo), followed by some overlapping thermal effects. It worth mentioning the endothermic effect with a peak at 482°C. For SIL2 sample, the DSC profile is more simple, consisting in aexotermic effect with onset at 308°C and peak at 347°C, immediately

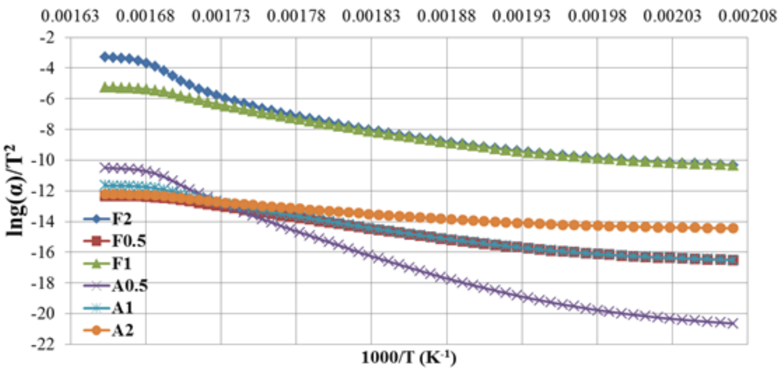


Fig. 4. DSC profile of SIL1 and SIL2 samples

followed by an endothermic peak at 408°C and two exothermic effects with peaks at 425 and 504°C.

All these experimental observations lead to the conclusion that thermal behaviour of the samples is different and probably the stability is modified by the aging of the silicone.

As last investigational method, a preliminary kinetic study was carried out using the Coats-Redfern (CR) method. CR method is a model-fitting one, where the conversion function can be expressed by Eq.1:

$$g(\alpha)=(1-\alpha)^n \qquad (1)$$

where:

g(α)-conversion function;

α-conversion degree;

n- reaction order.

CR expressions are presented in eq.2 and eq.3:

$$\ln\left[\frac{-\ln\ (1-\alpha)}{T^2}\right]=\ln\frac{A\cdot R}{\beta\cdot E}-\frac{E}{R\cdot T},\ \text{for n=1} \qquad (2)$$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2\cdot(1-n)}\right]=\ln\frac{A\cdot R}{\beta\cdot E}-\frac{E}{R\cdot T},\quad \text{for } n\neq 1; \qquad (3)$$

where:

T- temperature (K);

A- preexponential factor (min^{-1});

R- universal gas constant (8.314 $J\cdot mol^{-1}\cdot K^{-1}$);

β- heating rate ($K\cdot min^{-1}$);

E– activation energy ($kJ\cdot mol^{-1}$).

The graphical representation of lng(α)/T^2 *vs.* 1000·T^{-1} (figs. 4 and 5), linear dependencies are obtained for n=2 for both samples. The mathematical analysis of these linear dependencies (the slopes and the intercepts) lead to determination of characteristic values for E_a and lnA.

The results obtained by the Coats-Redfern kinetics, by assuming the dependence using six models are presented in table 1. As seen, in both cases, the best fitting model according to the values of R^2 was the one corresponding to a heterogenous decomposition of second order (n=2). For the analysed samples, the values for activation energies were 49.6 $kJ\cdot mol^{-1}$ for SIL1 and 57.6 $kJ\cdot mol^{-1}$ for SIL2.

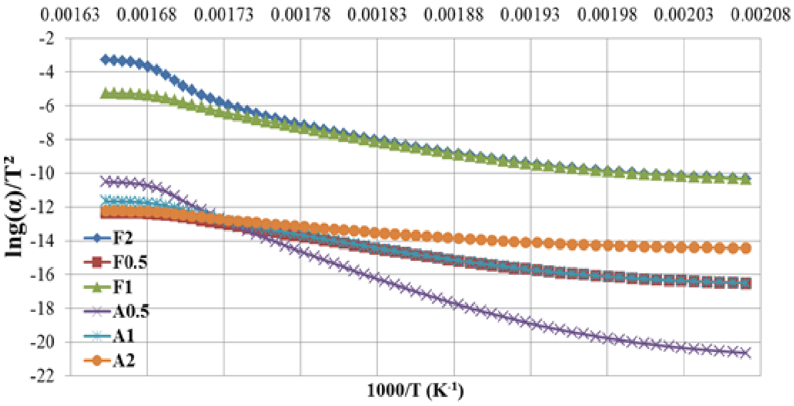


Fig. 5. Plotting of Coats–Redfern method for β=10 °C·min^{-1} for SIL1

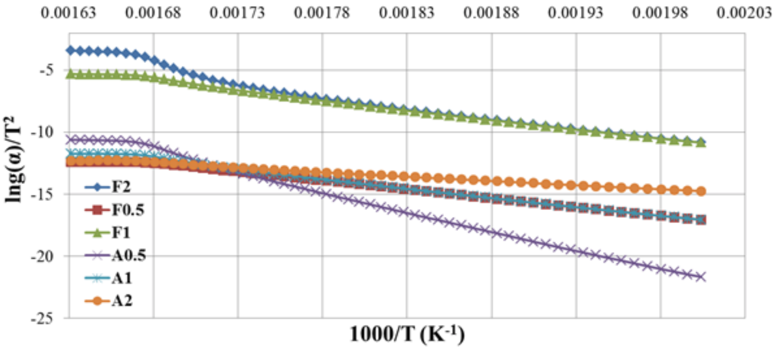
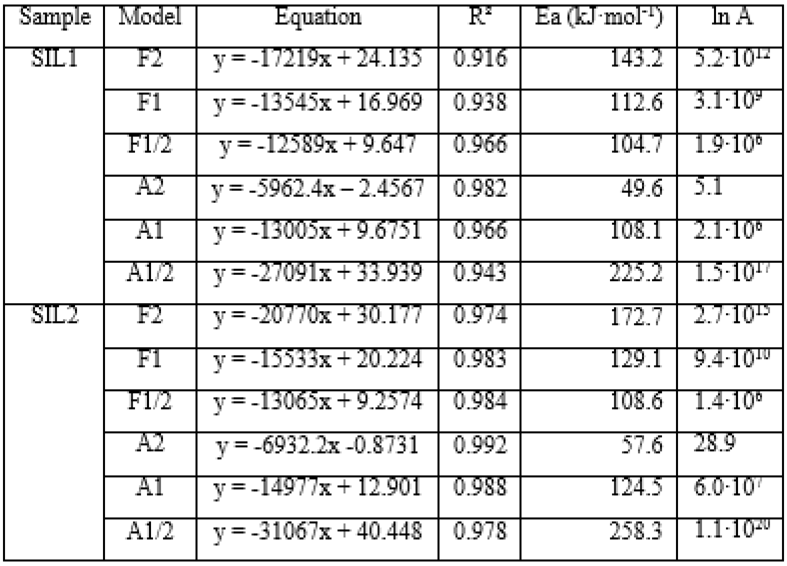


Fig. 6. Plotting of Coats–Redfern method for β =10 °C·min^{-1} for SIL2

Table 1
COATS-REDFERN KINETIC RESULTS FOR
SIL1 AND SIL2



Sample	Model	Equation	R^2	Ea (kJ·mol^{-1})	ln A
SIL1	F2	y = -17219x + 24.135	0.916	143.2	$5.2\cdot10^{12}$
	F1	y = -13545x + 16.969	0.938	112.6	$3.1\cdot10^{9}$
	F1/2	y = -12589x + 9.647	0.966	104.7	$1.9\cdot10^{6}$
	A2	y = -5962.4x – 2.4567	0.982	49.6	5.1
	A1	y = -13005x + 9.6751	0.966	108.1	$2.1\cdot10^{6}$
	A1/2	y = -27091x + 33.939	0.943	225.2	$1.5\cdot10^{17}$
SIL2	F2	y = -20770x + 30.177	0.974	172.7	$2.7\cdot10^{15}$
	F1	y = -15533x + 20.224	0.983	129.1	$9.4\cdot10^{10}$
	F1/2	y = -13065x + 9.2574	0.984	108.6	$1.4\cdot10^{6}$
	A2	y = -6932.2x -0.8731	0.992	57.6	28.9
	A1	y = -14977x + 12.901	0.988	124.5	$6.0\cdot10^{7}$
	A1/2	y = -31067x + 40.448	0.978	258.3	$1.1\cdot10^{20}$

Conclusions

Three investigational tools were used for a comparative analysis of two silicone samples used in maxillofacial prostheses. All investigations suggested some modification in the structure and as well stability of polymeric samples during aging. The Coats-Redfern kinetic model revealed for each sample a decomposition kinetics with a reaction order n=2, activation energies of 49.6 kJ·mol^{-1} for SIL1 and 57.6 kJ·mol^{-1} for SIL2 and preexponential factors also evaluated (5.1 for SIL1 and 28.9 for SIL2).

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