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Thermo-mechanical analysis of dental silicone polymers

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Abstract Soft lining materials are used to replace the inner surface of a conventional complete denture, especially for weak elderly patients, with delicate health who cannot tolerate the hard acrylic denture base. Most of these patients have fragile supporting mucosa, excessive residual ridge resorption, particularly on the mandibular arch. The application of a soft liner to the mandibular denture allows absorbing impact forces during mastication and relieving oral mucosa. Actually, the silicone rubbers constitute the main family of commercialised soft lining materials. This study was conducted to understand the relationships between the mechanical properties and the physical structure of polysiloxanes. For this purpose, a series of polysiloxanes of various chemical compositions have been investigated. The evolution of their physical structure as a function of temperature has been followed by differential scanning calorimetry (DSC). In order to facilitate comparisons, the mechanical modulus has been analysed upon the same heating rate using dynamic mechanical analysis (DMA). Polysiloxanes actually commercialised as soft denture liners are three-dimensional networks: the flexibility of chains allows a crystalline organisation in an amorphous phase leading to the low value of the shear modulus. The dynamic mechanical analysis shows that they are used in the rubbery state. So, polysiloxanes have steady mechanical properties during physiological utilisation.

Introduction

Soft lining materials are used to replace the inner surface of a conventional complete denture, especially for weak elderly patients, with delicate health, which cannot tolerate the hard acrylic denture base [1, 2]. Most of these patients have fragile supporting mucosa, excessive residual ridge resorption, particularly on the mandibular arch. Also, they have a lot of difficulties to wear a conventional complete denture: The biting forces lead to oral pain and mucosal wounds. The application of a soft liner to the mandibular denture allows absorbing impact forces during mastication and relieving oral mucosa. So, these weak patients feel more comfortable with soft lining complete denture, which realises a cushioning effect [3]. Soft liners constitute an attractive answer for the elderly population who increases such as the life expectancy.

Actually, the silicone rubbers constitute the main family of commercialised soft lining materials [1, 4–9]. In the literature, Baney et al. (1995), Takahashi et al. (2001) described silicon resin as being non-linear polymers reticulated from silsesquioxanes [10, 11]. Silsesquioxanes and silicon resins display a particular structural organisation, i.e. an amorphous random structure or an ordered structure as ladder, cage or partial cage.

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Many studies have been carried to describe their mechanical properties as adhesion to acrylic denture base, stress–strain behaviour, Shore A hardness or rupture and were completed by physico-chemical tests as water sorption or solubility [1, 12–18]. But, their interpretation at a molecular level was never considered. This study was conducted to understand the relationships between the mechanical properties and the physical structure of polysiloxanes.

For this purpose, a series of polysiloxanes of various chemical compositions have been investigated. The evolution of their physical structure as a function of temperature has been followed by differential scanning calorimetry (DSC). In order to facilitate comparison, the dynamic mechanical modulus has been analysed upon an analogous temperature scanning by dynamic mechanical analysis (DMA).

Experimental

Materials

All the tested polymers with their sample code, commercial name and chemical composition are listed in Table 1. Samples were produced in dental stone moulds according to prosthetic technique. Proportion, mixing and curing procedures were as recommended by product's manufacturers [1, 3, 12, 14]. Most recent polysiloxanes, namely RTV as room temperature vulcanisation polymerise at ambient temperature. Their processing needs to mix a same amount of two pastes. The muffle is filled into the mixture under a pressure of 300 bars at ambient temperature. To promote chemical reaction is possible to immerse the muffle was plunged into a water bath during 20 min at 45 °C. The HTV polysiloxane processing needs to fill into the muffle with one paste under a pressure of 250 bars. Then the muffle is submitted to a temperature cycle: a slowly temperature raising from ambient temperature to 100 °C, followed by 2 h at 100 °C, then air-cooled down to ambient temperature. After setting, samples were removed from the moulds in the open air, at ambient temperature.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry measurements were carried out with a DSC-7 Perkin Elmer instrument at a heating rate of 20 °C/min on 15–25 mg samples. The heat capacity C_p was recorded as a function of temperature T at atmospheric pressure. For all the samples a heating run was performed from –140 to 80 °C followed by a fast cooling from 80 to –140 °C. This thermal cycle is repeated one time. Then the samples were again fast cooled and a heating run was carried out from –140 to 0 °C for HTV and RTVg samples and from –80 to 0 °C for RTVp and RTVu samples. This last thermal cycle was repeated one time for HTV and RTVg samples and two times for RTVp and RTVu samples. The DSC thermograms exhibit three types of events:

- Endothermic peaks which express the melting of crystalline phase. The area under the peak represents the melting enthalpy ΔH_m; the maximum temperature represents the melting temperature T_m.
- Exothermic peaks associated to the crystallisation phenomena
- Step of the heat capacity, ΔC_p, associated to the glass transition phenomena. The glass temperature T_g is then defined as the midpoint of this heat capacity change in the heating run.

Dynamic mechanical analysis (DMA)

The mechanical properties of polysiloxane were investigated using an Rheometrics Scientific ARES strain controller rheometer in the torsion rectangular mode, using sample size of 44 × 11.5 × 1.5 mm. The maximal strain amplitude used was well within the linear viscoelasticity range for all the investigated samples. Dynamic storage modulus G', loss modulus G'' and loss factor $\tan \delta = G''/G'$ were measured as a function of temperature ranging from –140 to 80 °C at 3 °C/min at a different fixed angular frequency ranging

Table 1 Presentation of the series of polysiloxanes

Sample code: polysiloxane	Commercial name	Manufacturer	Chemical composition
HTV*	Molloplast®	Detax GmbH, Germany	Acetoxy-cure silicone + poly(methyl methacylate + γ-methacryloxy propyl trimethoxy silane
RTVg**	GC Reline®	GC Dental Products, Japan	Vinyl dimethylpolysiloxane + methyl hydrogen polysiloxane
RTVp**	Permafix®	Kohler GmbH, Germany	Polydimethylsiloxane with functional groups
RTVu**	Ufigel®	Voco GmbH, Germany	Mixing of several polyalkylsiloxanes

HTV* = high temperature vulcanisation; RTV** = room temperature vulcanisation from 10^{-2} to 100 rad s^{-1}. The isochronous evolution of the storage modulus G' and the loss factor tan δ are recorded as a function of temperature [7, 8, 17]. For each polymer, the following events will be identified:

- A mechanical relaxation associated with a first order transition (melting or crystallisation)
- A mechanical relaxation associated with the glass transition (T_g), namely the "dynamic" glass transition (T_α).

Results and discussion

Differential scanning calorimetry analysis

The physical structure is evidenced through the study of the transitions. Contrarily to other three dimensional polymers, polysiloxanes display an ability to show long range order due to the specific flexibility of the main chain. DSC curves presented on Fig. 1, show the influence of the chemical structure on the sample transitions. The DSC thermograms of all samples underline a step of heat capacity ΔC_p around –115 °C. Note that for the HTV polysiloxane, the break is more intense than for RTV polysiloxanes.The glass temperature T_g and ΔC_p characterise the amorphous phase. Their values are listed in Table 2. All RTV polysiloxanes show a smaller ΔC_p: that can be understandable by a smaller steric hindrance of side chains.

Around –90 °C, for HTV, RTVg and RTVu polysiloxanes, an exothermic peak, associated with a cold crystallisation, is observed when the sample is quenched from the rubbery state. This peak is less intense for RTVu polysiloxane: Table 2 reports a lower crystallisation enthalpy ΔH_c. The behaviour of these polysiloxanes is similar to the one of linear polymer like PET and PEEK [19, 20], which are well known for crystallisation kinetics lower than the usual cooling rate. Low crystallisation kinetics in the above cited polysiloxanes might be related to their chemical

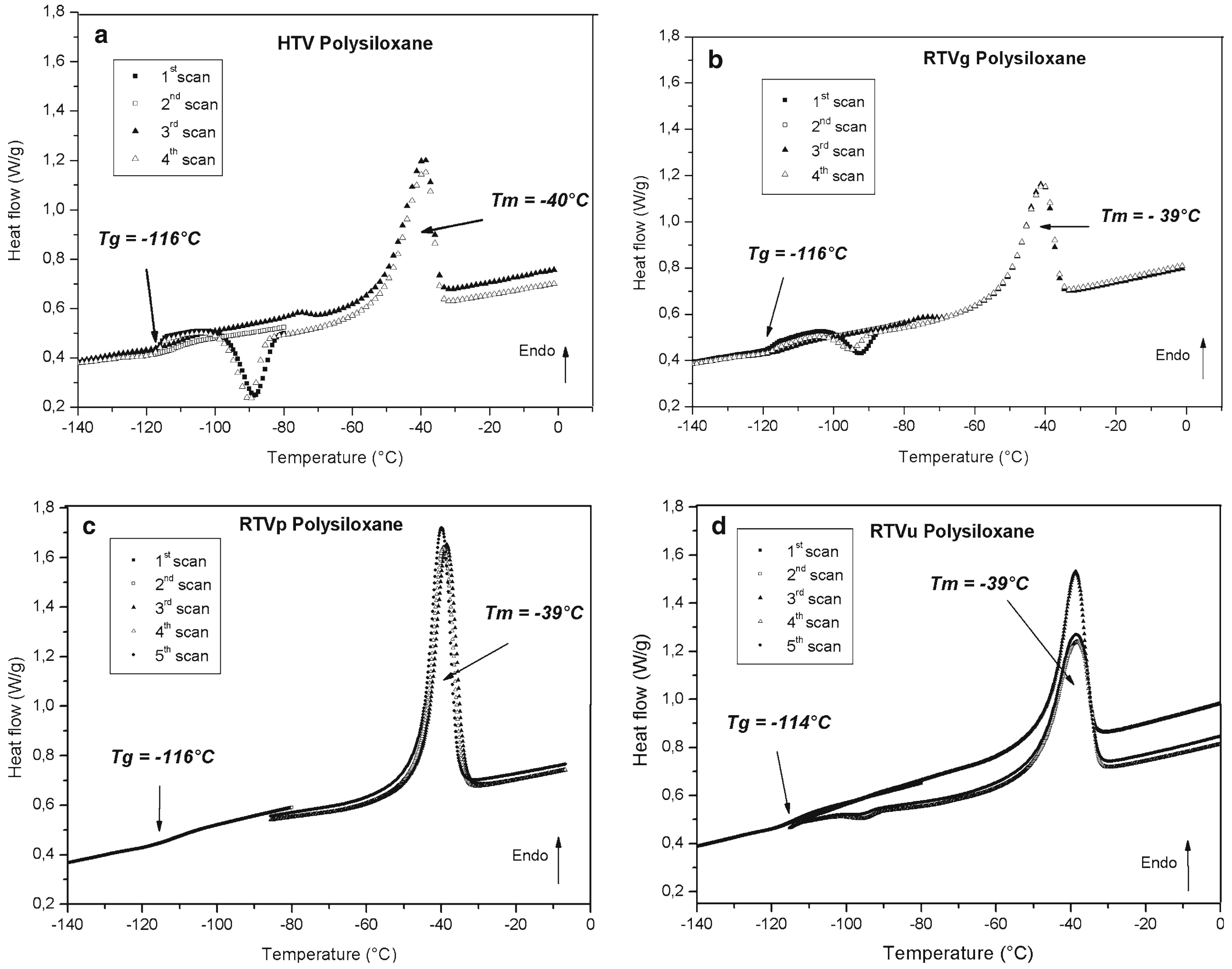

Fig. 1 DSC thermogramms of polysiloxanes: (**a**) HTV; (**b**) RTVp; (**c**) RTVg; (**d**) RTVu

Table 2 Characteristic parameters of transitions (glass transition, crystallisation, melting) for polysiloxanes

Polysiloxanes	T_g (°C)	ΔC_p (J g^{-1} °C^{-1})	T_c (°C)	ΔH_c (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})
HTV	–116	18×10^{-2}	–90	–8.4	–40	17.7
RTVg	–116	8×10^{-2}	–90	–5	–39	15.5
RTVp	–112	7×10^{-2}	–	–	–40	22.5
RTVu	–114	10×10^{-2}	–93	–0.32	–39	19

structure: HTV, RTVg and RTVu possess large side chains with of course important steric hindrance. No exothermic peak is recorded for RTVp polysiloxane. This means that its crystallisation kinetic is always faster than the cooling rate. This result can be explained by the chemical structure of this polydimethylsiloxane, which presents a regular structure with sole methyl groups with small hindrance.

Around –40 °C, for all polysiloxanes, the endothermic peak indicates a melting. The melting peak of RTVp polysiloxane is the most intense, tight and reproducible since the crystallisation is totally achieved before the run. The other polysiloxanes show broad melting peaks revealing a less regular organisation due to the chemical structure but also to the two steps (hot and cold) crystallisation procedures. The characteristic parameters of melting, i.e. melting temperature T_m and melting enthalpy ΔH_m are listed in Table 2.

Dynamic mechanical relaxations

The DMA thermograms (Fig. 2) underline the various mechanical relaxations associated with transitions. The mechanical behaviour can be foreseen for each polysiloxane at different temperatures. For temperatures below –115 °C, for all polysiloxanes, the storage modulus G' is constant. The value of the elastic modulus is near from 1 GPa: the glassy plateau is characteristic of an elastic behaviour.

From –115 to –100 °C, the storage modulus falls down to 0.5 MPa: a mechanical relaxation associated with glass transition is observed. From –100 to –50 °C, the storage modulus decreases slowly with temperature. The behaviour of polysiloxanes in this temperature range is viscoelastic. The temperature T_α corresponding to the tan δ loss factor maximum (near –115 °C) is the mechanical relaxation temperature. Since the molecular origin of this mechanical relaxation is the glass transition, T_α remains of the same order of magnitude than the glass transition temperature T_g.

Around –40 °C, the storage modulus decreases steeply down to 2 MPa due to melting. The $T_{\alpha'}$ temperature corresponding to the tan δ loss factor maximum near –40 °C is practically the melting temperature.

Beyond –40 °C, the storage modulus is constant: the value of the rubbery modulus is near 1 MPa. Polysiloxanes have a rubbery behaviour with an unlimited rubbery plateau.

In order to compare the mechanical behaviour of the investigated samples, the storage modulus of all polysiloxanes have been reported on the same thermogram (Fig. 3). They all show the same mechanical behaviour. However, some the differences can be pointed out as follows: HTVp polysiloxane shows the highest value of glassy modulus (>1 GPa) and also, the smallest value of rubbery modulus (<1 MPa). Such values can be explained by the flexibility of main chains allowing an easy organisation.

In the range of physiological temperature (around 37 °C), the mechanical behaviour of polysiloxanes is steady since it corresponds to the rubbery plateau. It is interesting to compare the obtained data with the ones of literature. Buch, Waters et al. and Saber-Sheikh et al. [7, 8, 17] performed experiments in more restricted temperature range (from –100 to +150 °C, from +30 to +70 °C, from +15 to +55 °C). So, the comparison is limited to the values around the physiological temperature of 37 °C. It is interesting to note the good consistency between the various sets of data.

Physical structure and mechanical properties relationships

The mechanical relaxation temperatures, associated with glass transition T_α and melting $T_{\alpha'}$ recorded by isochronal DMA at 1 rad s^{-1}, have comparable values with the glass and melting temperatures T_g and T_m recorded by DSC. The molecular mobility liberated by the breaking of physical interactions at the glass transition is responsible for the corresponding mechanical relaxation. For RTVp polysiloxane, the storage modulus G' is measured as a function of temperature for two fixed frequencies (1 and 100 rad s^{-1}) (Fig. 4). For temperatures below –36 °C, the relaxation processes are independent of the frequency: the melting of the crystalline phase of a polymer is well a first order thermodynamic transition as expected. For higher temperatures, the three-dimensional network prevents the flow.

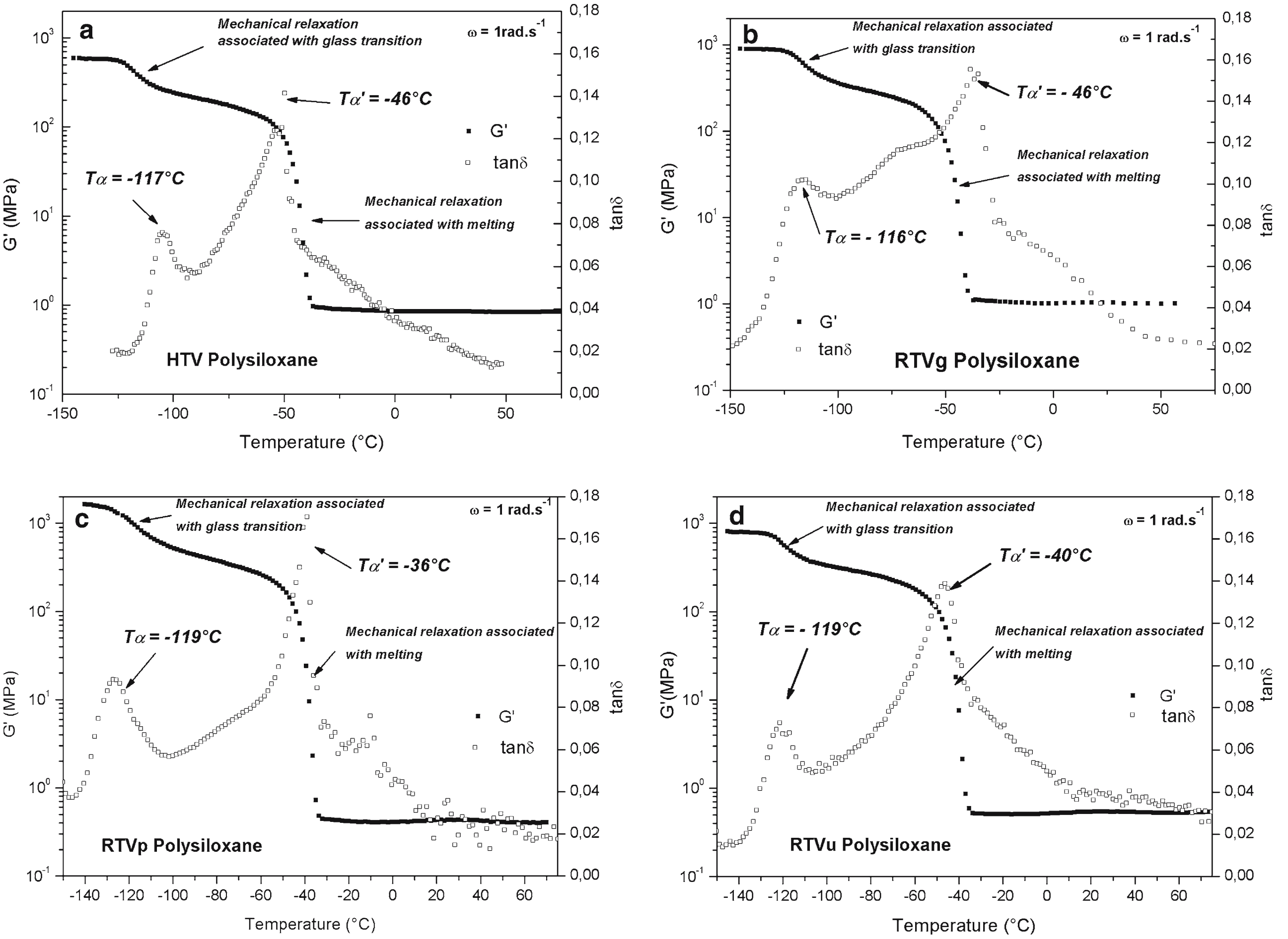

Fig. 2 Temperature dependence of *G′* and tan *δ* at 1 rad s^{-1} for polysiloxanes: (**a**) HTV; (**b**) RTVp; (**c**) RTVg; (**d**) RTVu

For temperatures around –115 °C, the observed relaxations are dependent upon frequency: the viscoelasticity of amorphous phase is linked to the pseudo second order transition (glass transition). At the physiological temperature of 37 °C, RTVp polysiloxane has a rubbery behaviour, whatever the frequency is. For temperatures higher than melting temperature, the storage modulus of polysiloxanes is constant: this is

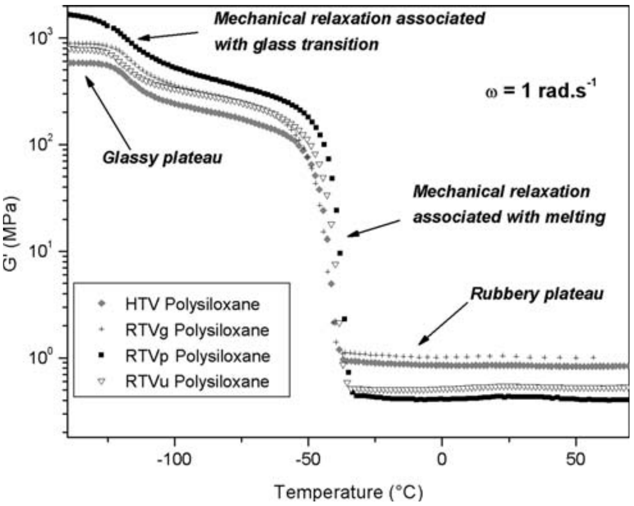

Fig. 3 Comparative temperature dependence of *G′* at 1 rad s^{-1} in polysiloxanes

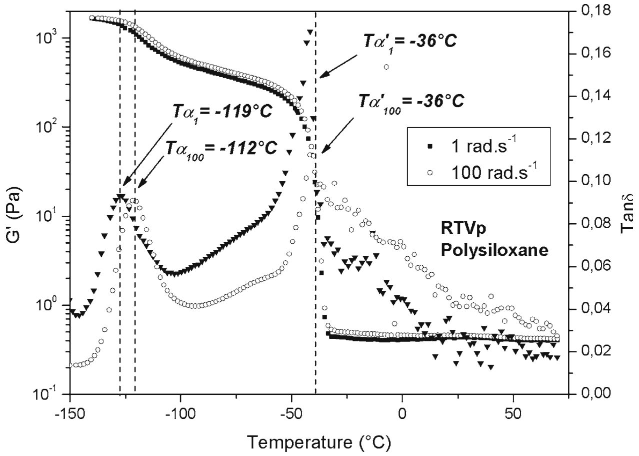

Fig. 4 Influence of the angular frequency on the temperature dependence of *G′* and tan *δ* in RTVp polysiloxanes

a characteristic of the rubbery plateau. Also, the viscoelastic behaviour (from –118 to –40 °C) is far from the area of use.

Conclusion

Relationships between physical structure and mechanical properties allow the understanding of mechanical behaviour around working temperature as well as the physical ageing. Polysiloxanes actually commercialised as soft denture liners are used in the rubbery state. They are three-dimensional networks, which show steady mechanical properties during physiological utilisation. The flexibility of chains allows a crystalline organisation in an amorphous phase, and is also at the origin of the low shear modulus value.

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