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Characterization of commercial soft liners by dynamic mechanical analysis

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Although there is a significant clinical interest in suitable polymer-based soft liners, none have proven fully satisfactory in actual use. As a result there has been continued interest in the development of new materials. One major weakness in the development of improved materials has been the lack of clear understanding of structure/property relationships. This paper deals with the determination of visco-elastic properties such as E' (Storage modulus) and tan δ (damping factor) of four commercial materials. They represent the broad range of chemical types available for denture base soft liners. A DMA study of four materials: (1) Molloplast B (silicone); (2) Novus (phosphazine); (3) Kurepeet (fluropolymer); and (4) Super Soft (acrylic) was made using a Perkin-Elmer DMA-7. Samples were made following the manufacturers' instructions, in the form of sheets 1.5 mm thick and 15.0 mm square. The samples were tested compressively using a 3 mm flat tip probe cycled at a frequency of 1 Hz. Wet and dry specimens were evaluated for E' and tan δ over a 5–95 °C temperature range. Water sorption was determined gravimetrically at 37 °C. Changes in E' between the wet and dry conditions for Molloplast (B), Kurepeet and Super Soft were insignificant. A significant increase in tan δ for wet Novus was observed, suggesting that the material is capable of dissipating more energy. The 'wet' modulus (E') is about 42% lower than the "dry" modulus (E'). This difference may be attributed to the very high water sorption (34%) of Novus. i.e. the significant decrease in E' indicates plasticization due to sorbed water. Changes in visco-elastic properties seem to occur for materials which take up large amounts of water at 37 °C. DMA is found to be a useful supplement for the evaluation of soft lining materials in conjunction with the standard mechanical test methods.

1. Introduction

There is significant clinical demand for the availability of denture soft lining materials as an aid in the treatment of painful, localized tissue irritation under dentures [1–6]. A number of different types of materials have been tried for this application, but none has proved fully satisfactory. Commonly observed deficiencies include poor adhesion to the denture base, poor tear resistance, difficult finishing and polishing, excessive hardness, gradual hardening with time [1–3], and excessive fluid absorption with resultant distortion and fouling. Fortunately, no one material exhibits all of these faults, but certain problems are characteristic of particular materials.

Most soft lining materials can be classified broadly into two types, namely silicone elastomers and plasticized soft acrylics. The properties and defects together with chemical structure of these materials have been well documented [1–3]. While acrylic materials have excellent adhesion to poly(methyl methacrylate), they have poor elastic properties and harden gradually due to leaching out of plasticizers. Although silicone soft liners have excellent elastic properties, they are greatly susceptible to deterioration in the oral environment.

In particular, silicone polymers suffer from poor tear resistance, poor adhesion to poly(methyl methacrylate) dentures [7], and depending on their detailed chemical composition [8, 9] may support the growth

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of candida albicans [8]. Usually, these silicones are of the condensation type. It is known that some silicone soft liners take up more than 50 wt % water [5]. Since water uptake of elastomers is largely governed by water-soluble impurities [10], silicones can be worse than any other polymers.

So-called soft acrylics usually owe their compliance to the presence of a plasticizer, commonly a phthalate, although phosphates have been used. Composition of a number of such materials has been thoroughly reviewed [4] and the hardening of the liner has been invariably attributed to the loss of plasticizers. At the same time, the presence of a plasticizer increases the tendency of the material to dissolve organic compounds and to discolour. However, the adhesion to poly(methyl methacrylate), not surprisingly, is generally good.

Of the commonly used types, silicone-based materials are most likely to have difficulty with adhesion, finishing, or tear resistance [1, 3], while plasticized acrylics are often judged to be too hard, to harden further with time and to suffer from excess water sorption [5, 11–15]. In spite of the periodic introduction of new and supposedly improved products, no general solution to these problems has been found. These problems with the most popular materials have led manufacturers to introduce alternative compositions. Among the recent introductions are materials based upon poly phosphazines [16] and fluoropolymers [7].

Measurements of viso-elastic properties must be a central aspect of evaluation of polymeric-based materials such as soft liners, from the viewpoint of their performance and elucidation of the influence of molecular structure. Such properties of some soft liners have been admirably detailed by Braden *et al.* [18, 19].

This research is part of a programme for the development of improved soft lining materials based on the determination of acceptable property ranges from the characterization of the best available current products, investigation of the property–composition–structure relationships for the major types of materials, and the preparation of new formulations incorporating the desired characteristics. This paper presents results from the characterization of four chemical types of commercial soft liners. Additional data on these materials have been presented elsewhere covering commonly measured properties [20]. The results obtained by dynamic mechanical analysis, which is being used to supplement the traditional methods, are presented here. Later portions of this research programme will involve the development and testing of new soft liners. The result of these characterization tests will be used to establish minimal standards of acceptability for the new materials. The fundamental problem is either to confer good adhesion and tear resistance on silicone polymers or to formulate soft acrylics that do not contain leachable plasticizer.

2. Experimental procedures

In order to obtain broadly based information on the characteristics of currently available commercial products, four commercial soft liners were selected, each representing a different type of material. These products are listed in Table I.

Each of these products (plus three additional materials) had been previously evaluated for water sorption/desorption, durometer hardness, tensile strength, tear strength, and peel strength [20]. The four products tested here were selected as representative of the available ranges of both composition and properties.

The dynamic mechanical analyses were performed using a Perkin-Elmer DMA-7 Thermal Analysis System. This instrument has several design features which make it particularly useful for testing soft liners and other dental products. It is capable of operating in a compression cycling mode with a wide variety of probe tips, and permits operation with the specimen in air or immersed in water. An attempt was made to adjust the conditions of test to approximate, where possible, the normal conditions of use. The specimens were prepared in accordance with the manufacturer's processing instructions and in the form of flat sheet 1.5 mm thick and 15 mm square. They were supported on a rigid plate and loaded with a flat-ended probe 3 mm in diameter. The probe was adjusted to maintain a static stress of 5×10^4 Pa with a superimposed dynamic stress of 5×10^3 Pa at a frequency of 1.0 Hz.

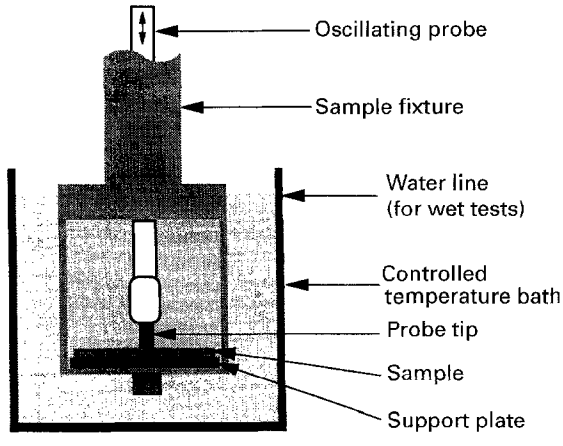

Figure 1 Schematic drawing showing the arrangement of the test apparatus.

TABLE I Commercial soft liners evaluated

Product	Material type	Source
Molloplast B	Heat-cured silicone	Detax/Karl Huber GmbH & Co. KG, Germany
Novus	Polyphosphazine	Hygienic Corp., Akron, Ohio, USA
Kurepeet	Fluoroelastomer	Kureha Chemical Ind. Co., Tokyo, Japan
Super soft	Plasticized Acrylic	Coe Laboratories, Chicago, Illinois, USA

TABLE II Dynamic mechanical analysis test conditions

Equipment	Perkin-Elmer DMA-7 Thermal Analysis System	
	Probe-3 mm diameter, flat tip	
Specimen	Flat sheet-15 mm square, 1.5 mm thick	
Conditions	Wet and Dry	
	Temperature range:	5–95 °C
	Temperature rate:	2.5 °C/min
	Static stress	5×10^4 Pa
	Dynamic stress	5×10^3 Pa
	Frequency	1.0 Hz

Specimens were tested in both the wet and dry conditions. The wet specimens had been preconditioned in 37 °C water to constant weight, or for a minimum of 100 days for those specimens which failed to equilibrate. "Dry" specimens were tested in air while "wet" specimens were tested in distilled water. Each test run consisted of measurements made while heating the specimen from 5 °C to 95 °C at 2.5 °C/min. A schematic drawing showing the arrangement of the test apparatus is shown in Fig. 1 while the test conditions are summarized in Table II.

3. Results

The results are obtained in the form of graphs of storage modulus (E') and loss tangent (tan δ) versus temperature for each run. It is possible to superimpose the results from separate runs on the same graph thus facilitating direct comparison of different materials or test conditions. An example of such a comparison is shown in Fig. 2, where the results for wet and dry Super Soft are compared. These results are characteristic of the plasticized acrylic materials. A vertical line has been inserted at 37 °C as an aid in evaluating the properties of the material under the conditions of use. The corresponding results for Moloplast B are shown in Fig. 3. Such results are characteristic of most silicone-based soft liners.

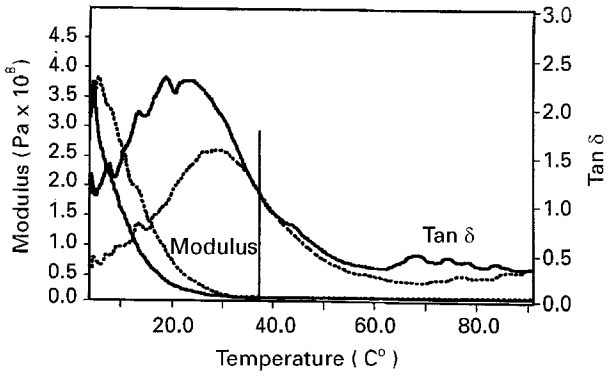

Figure 2 DMA traces of storage modulus (E') and loss tangent (tan δ) in the temperature range 5–95 °C for Super Soft in "dry" (···) and "wet" (—) conditions.

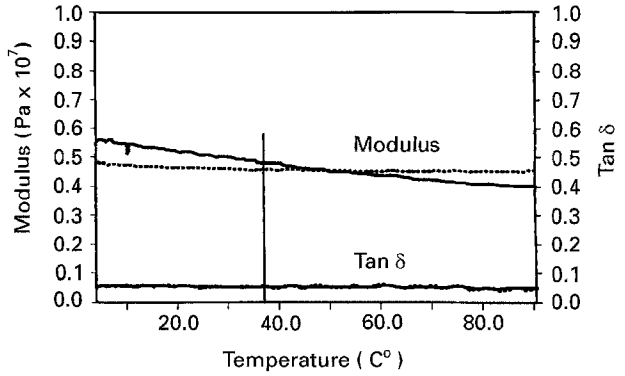

Figure 3 DMA traces of storage modulus (E') and loss tangent (tan δ) in the temperature range 5–95 °C for Molloplast B in "dry" (···) and "wet" (—) conditions.

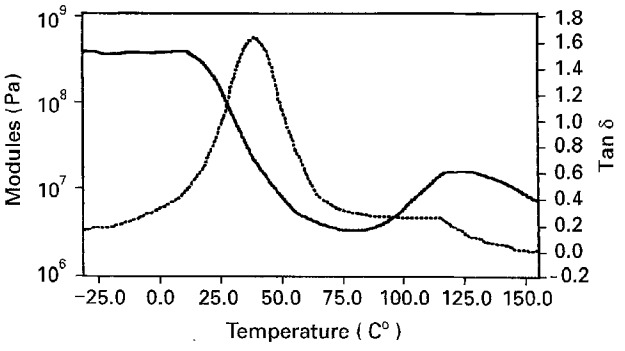

Figure 4 DMA traces of storage modulus (E') (—) and loss tangent (tan δ) (···) in the temperature range −30 °– + 150 °C for Super Soft in "dry" conditions.

The differences between these two sets of curves, particularly in their response to changes in temperature, can provide significant information about the structure and likely behaviour of the materials. However, when comparisons are to be made among several products, it is often more convenient to tabulate the properties under the expected conditions of use. Table III is such a tabulation of the properties of the four materials evaluated in this study at body temperature (37 °C).

Fig. 4 presents the storage modulus and loss tangent measurements from an independent test of an additional dry Super Soft specimen tested over an extended temperature range from −30 °C to 150 °C. Such tests can provide supplemental information to distinguish between curve deflection caused by glass transitions and melting.

TABLE III DMA properties at 37 °C

Material	Chemical type	Modulus E' (MPa)		Damping tan δ		Water sorption
		Dry	Wet	Dry	Wet	
Molloplast B	Silicone	4.8	5.1	0.005	0.005	0.5
Novus	Polyphosphazine	6.2	3.5	0.12	0.10	34.0
Kurepeet	Fluoroelastomer	5.0	5.0	0.5	0.75	2.0
Super Soft	Plasticized Acrylic	10.0	8.0	1.25	1.25	5.0

4. Discussion

The results of DMA provide valuable information not readily obtained by other methods. It is particularly useful in characterizing soft liners, and shows clear differences among the products tested here. A special advantage is the broad overview of behaviour provided by its temperature scanning approach. At the same time it cannot address directly certain important clinical performance characteristics such as tear resistance or peel strength. DMA does seem to be a very valuable adjunctive method particularly as a guide to characteristics and temperature ranges meriting more intensive investigation by other methods.

These advantages are well exemplified in the comparison of the two most popular types of materials, the plasticized heat cured acrylics and the heat-cured silicones, representatives of which were tested here. The traces obtained for Super Soft (Fig. 2) are considered characteristic of materials exhibiting a glass transition in the temperature range investigated. At low temperatures the measured storage modulus values are relatively high but show a rapid decrease to low levels as the glass transition temperature is approached. At the same time the damping coefficient, tan δ, starts low, rises to a peak, and then declines again. The glass transition is normally interpreted as lying in the temperature range between these two transitions, near 15–20 °C in this instance.

The correspondence of the DMA curves to particular transformations within the material is ultimately dependent upon correlations with the results from other test methods such as determinations of the coefficient of thermal expansion or the specific heat. This correlation is normally done only once for particular types of material and not for each material tested. For example, the identification of the transition shown in Fig. 2 as a glass transition rather than a melting range is based on experience with such external correlations. An additional method of potential discrimination can involve an extension of the temperature range evaluated. Fig. 4 shows the results for DMA on a separate Super Soft specimen extending both above and below the normal 0–90 °C range.

Comparison of Figs 2 and 4 show several points of interest. First, the changes in modulus and tan δ seen in Fig. 2 are confirmed for the additional sample of Fig. 4. Second, at low temperatures no changes are seen, the measured values remaining the same as those for 0 °C, thus indicating no transitions within this range. Third, and most interesting, increasing the temperature range to 150 °C discloses an additional transformation starting at 120 °C. The modulus increase and loss tangent decrease is characteristic of a transformation such as crosslinking and is so interpreted here. The occurance of this change, which could not occur above the melting point, clearly identifies the transition at 15–20 °C as a glass transformation.

A comparison of the "wet" and "dry" pairs of curves in Fig. 2 clearly reflects the effect of water sorption on Super Soft which absorbs 5% water when saturated at 37 °C. The overall effect is to soften the material and to reduce the glass transition temperature. The "wet" modulus is lowered at all temperatures and the high–low transition occurs at a lower temperature. For the "wet" conditions, damping is increased with the tan δ being higher and occurring at a lower temperature.

A major advantage of the DMA method lies in its ability to examine the temperature dependence of such transitions with limited numbers of specimens. Most conventional mechanical test methods, such as tensile tests or tear tests, require the use of multiple specimens to achieve statistical significance. This has led most specification testing and product comparisons to be done at only one temperature. For dental products the temperature most commonly selected is the temperature of use, 37 °C. This limitation can conceal important differences in the effect of other variables.

For Super Soft, test made only at 37 °C show relatively little difference between the wet and dry conditions (see Fig. 2 and Table III). Both modulus curves lie at low values at that temperature while the two tan δ curves coincidentally lie very close together because the shifts of the "wet" curve to higher values and lower temperatures largely compensate for each other at that point. In contrast, the DMA results clearly depict the plasticizing effect of water.

The results for the heat cured silicone Molloplast B shown in Fig. 3 are quite different. Neither the modulus nor tan δ curves show significant variation across the temperature range indicating that no glass transition occurs in this range. Molloplast B is highly crosslinked and its total water sorption is low. For these reasons the effect of water sorption on the properties is limited. No changes are seen in damping, while the modulus of the wet specimens increases at low temperatures and decreases at high temperatures. The wet specimens show little average change in modulus, but a greater rate of decline with increasing temperature. The low temperature increase in modulus has been interpreted as resulting from a stressing of the crosslinked network resulting from the insertion of water molecules into limited intermolecular spaces.

The results for the other two materials show many similarities to the products already discussed. Kurepeet appears to exhibit a glass transition temperature near 10 °C although the tan $^{\varepsilon}$ peaks are somewhat confused by the proximity to the starting temperature for the run. The damping of the "wet" specimens remains higher than that of the "dry" specimens throughout the temperature range. Novus, like Molloplast B, shows no glass transition. The damping curves show little variation with temperature in either the "wet" or "dry" conditions. Similarly, the modulus curves show only a slow decline with increasing temperature. However, the "dry" modulus is about 75% higher than the "wet" modulus. This difference apparently results from the very high water sorption (34%) of Novus.

In spite of the great chemical differences among these products, the actual range of DMA properties is quite limited. As shown in Table III, at 37 °C the range in modulus is from 4.8 to 10.0 MPa dry and from 3.5 to 8.0 MPa wet. The tan δ values both wet and dry lie in the range 0.05 to 1.25. Within these

ranges we have no criteria for believing that higher or lower values are preferable. Assuming that design modifications by the manufacturers based on clinical acceptance have resulted in convergence on a commercially acceptable range, these values seem appropriate initial screening ranges for experimental materials.

Similar guidelines can be derived from the other mechanical property test results. In general the measured values formed relatively coherent groups, and the only property for which there was any significant difference was water sorption where the value for Novus exceeded thirteen times the mean for other products. Although not yet confirmed clinically, this high water sorption appears associated with excessive dimensional change. Nevertheless, bearing in mind the example provided by soft lenses, it is probably inappropriate to condemn this product on this basis alone unless the concomitant dimensional changes are associated with clinical problems in regard to fit.

5. Conclusions

Based on these findings we have concluded that dynamical mechanical analysis is a useful supplement for use with the standard mechanical test methods for the evaluation of soft lining materials. The instrument design and mode of operation seem to be important in this use.

Using this approach significant variations can be measured among the different types of products tested.

The useful range of a series of mechanical properties has been determined for a number of commercially successful products and used to establish tentative target ranges for new materials.

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