JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 7 (1996) 237–240

Dynamic mechanical analysis and water sorption of some experimental elastomeric soft lining materials

S. KALACHANDRA
NSF Science and Technology Center, Department of Chemistry, Virginia Tech, Blacksburg, VA 24061-0212, USA; Operative Dentistry, Dental Research Center, University of North Carolina, Chapel Hill, NC 27599-7450, USA

D. XU
NSF Science and Technology Center, Department of Chemistry, Virginia Tech, Blacksburg, VA 24061-0212, USA

S. PARKER, P. RIGGS
Department of Biomaterials in Relation to Dentistry, Dental School, The London Hospital Medical College, London E1 2AD, UK

D.F. TAYLOR
Operative Dentistry, Dental Research Center, University of North Carolina, Chapel Hill, NC 27599–7450, USA

M. BRADEN
IRC in Biomedical Materials, The Institute of Orthopaedics, Royal National Orthopaedic Hospital, Stanmore, Middx. HA7 4LP, UK

This research was undertaken to develop a better understanding of the relationships among the compositions, structures and properties of denture soft liners. Five butadiene–styrene–acrylic elastomers were prepared. They were prepared using 50% of powdered prepolymerized butadiene–styrene polymer combined with 50% of a methacrylate monomer (HMA or EHMA) plus varying amounts of initiator and crosslinker. The mixtures were gelled and processed conventionally. Specimens were then committed to dynamic mechanical analysis and water sorption. Dynamic mechanical analysis was performed over the temperature range 5–95 °C at the rate of 2.5 °C/min using a Perkin Elmer DMA-7 with 3 mm flat tip probe at 1 Hz. Wet and dry values for storage modulus (E') and damping factor (tan δ) were determined at 37 °C. Water sorption of these butadiene styrene elastomer–acrylic systems from solutions of varying concentrations was measured in order to establish the role of osmotic pressure. Diffusion coefficient (D_d) was determined from the desorption values. The relatively lower values of D_d observed in most highly concentrated solutions particularly 1 M sodium chloride and glucose may be interpreted as related to reduced water sorption from these solutions. Increasing crosslinking increased the modulus and decreased water sorption. Using hydrophobic EHMA instead of HMA reduced water uptake, reduced dry modulus and reduced the decrease in modulus caused by water sorption. Dynamic moduli and water sorption generally exceeded those of the commercial materials studied. For all experimental materials, water uptake from saline and glucose solutions confirmed that the diffusion process is osmotically driven.

1. Introduction

A soft lining is a compliant material placed between the hard denture and the oral mucosa in order to treat or avoid the development of local areas of soreness under dentures [1–4]. These materials ensure a more even distribution of the forces imposed during use, absorb energy and reduce the displacement of mucosa, thus improving the comfort of the patient. Because of deficiencies in presently available materials there is still a significant clinical demand for improved soft liners as an aid to treatment of denture patients [5–11].

Many current materials suffer from a variety of problems. Silicone-based materials can fail due to poor adhesion to acrylic dentures [10], candida growth [12] and/or low tear resistance [13]. Soft

0957–4530 © *1996 Chapman & Hall*

acrylic materials may harden where plasticizer loss is involved. In order to overcome this hardening problem, polymerizable plasticisers have been used in place of phthalate esters but some resulting materials suffered long-term water uptake [14]. Newer materials of very different compositions also suffer similar problems, Novus (a polyphosphazine fluoroelastomer) has high water uptake [15], Molloplast b (a silicone–methacrylate adduct) and Kurepeet (a fluoroethylene elastomer) have poor tear strength [15].

The current research is part of a collaborative program for the development of improved soft lining materials involving evaluation of experimental materials using a variety of less frequently used methods. Several typical commercial products have been evaluated as standards [15]. The present paper deals with the characterization of five experimental materials formed by gelation of butadiene–styrene prepolymers with higher acrylic monomers. After processing, the materials were evaluated by dynamic mechanical analysis (DMA) in both dry and wet conditions. Water uptake from distilled water and aqueous solutions at 37 °C, and diffusion coefficients at that temperature were determined. The results for these experimental materials were compared with the DMA data for four proprietary soft lining materials already published [15].

2. Experimental Procedures

The basic polymer used in this study was a 70/30 butadiene–styrene block copolymer and the monomers were n-hexyl methacrylate (HMA) and ethyl hexyl methacrylate (EHM) and ethylene glycol dimethacrylate (EGDM) as crosslinking agent. The initiators were lauryl peroxide (LP) and benzoyl peroxide (BP). The benzoyl peroxide was premixed 50/50 phthalate (Lucidol CH 50, AKZO Chemicals Ltd). The formulations prepared from these ingredients are shown in Table I.

2.1. Specimen preparation

Doughs were prepared from a 50/50 wt/vol mixture of the butadiene–styrene copolymer and the appropriate monomer. They were pressed into 1.5 mm thick sheets in metal moulds and cured in a water bath. The curing cycle involved heating from room temperature to 100 °C over 30 min followed by an additional 30 min at 100 °C. 15 mm square samples were cut from the sheets for DMA and 20 mm square samples for water sorption.

TABLE I Formulations

Code	Monomer	Initiator
A	HMA + 0.5% EGDM	0.5% BP
B	HMA + 0.5% EGDM	1.0% LP
C	EHMA + 1.0% EGDM	0.5% BP
D	EHMA + 0.5% EGDM	1.0% LP
E	EHMA + 1.0% EGDM	1.0% LP

2.2. Dynamic mechanical analysis (DMA)

Storage modulus (E') and the loss tangent (tan δ) were determined during heating over the temperature range 5–95 °C at a rate of 2.5 °C/min using a Perkin Elmer DMA-7 system at 1 Hz in the compressive mode. A flat-tip 3 mm diameter probe was used as described in an earlier report [15].

2.3. Water sorption

Water sorption, desorption, and diffusion coefficient (D_d) were determined at room temperature. Samples were predried, weighed and then immersed in liquid with periodic weighing until equilibrated (37 °C). They were then redried in a desiciator with weighing at various intervals of time. The liquids used were distilled water; 0.1 M, 0.3 M, and 1 M solutions of glucose and NaCl; and artificial saliva (Xero-Lube). Details of the procedure have been previously reported [16–18].

3. Results

3.1. Dynamic mechanical analysis

DMA results for storage modulus (E') and loss tangent (tan δ) were measured for both wet and dry specimens over the 5–95 °C range. A representative DMA trace is shown in Fig. 1. For comparison of materials, the E' and tan δ values at 37 °C are given in Table II. These values were determined as the intersections of the traces with a vertical line drain at 37 °C. Also included in the table are glass transition temperatures and water sorptions.

3.2. Water sorption

Results for water sorption are included in Tables II and III and in Fig. 2. Table III includes the results for distilled water and for each of the sodium chloride and glucose solutions, and provides the basis for the discussion of osmolality as the controlling factor in water sorption.

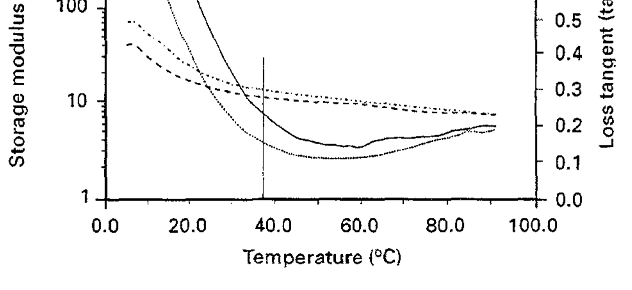

Figure 1 Typical dynamic mechanical analysis (DMA) traces from 5–95 °C for formulation "A" in dry and wet conditions: — tan δ (dry); –·– modulus (dry); ---- tan δ (wet); – – – modulus (wet).

TABLE II DMA properties

Formulation	Modulus (MPa)		Loss tangent		T_g(°C)		Water sorption (37°C) (wt %)
	Dry	Wet[a]	Dry	Wet[a]	Dry	Wet[a]	
A	14.0	11.9	0.25	0.16	11	5	7.3
B	19.2	11.6	0.21	0.17	9	7	7.1
C	19.9	15.1	0.36	0.27	19	13	5.8
D	15.9	13.0	0.34	0.32	15	13	5.4
E	20.9	16.0	0.37	0.29	20	17	5.0
Molloplast b	4.8	5.1	0.05	0.05	> 100	–	0.5
Super Soft	10.0	8.0	1.25	1.25	15–20	–	5.0

[a] Preconditioned to constant weight at 37 °C

TABLE III Water sorption data from distilled water, sodium chloride, glucose solutions and artificial saliva

Formulation	Property	Water	NaCl			Glucose			Artificial saliva
			0.1 M	0.3 M	1.0 M	0.1 M	0.3 M	1.0 M	
A	Sorption (%)	5.4	2.8	1.7	0.8	4.3	2.9	1.2	4.5
	Desorption (%)	7.3	4.6	3.6	2.9	4.9	4.0	2.7	4.3
	$D_d \times 10^8$ (cm^{2}s^{-1})	4.2	4.5	4.4	1.5	4.7	5.1	3.5	5.3
B	Sorption (%)	5.0	3.1	1.6	0.7	4.1	2.7	1.1	4.9
	Desorption (%)	7.1	5.0	3.4	2.8	5.3	3.9	2.4	4.6
	$D_d \times 10^8$ (cm^{2}s^{-1})	4.1	4.2	3.4	1.2	4.4	4.8	2.9	4.6
C	Sorption (%)	3.6	2.3	1.2	0.3	2.2	1.7	0.8	3.4
	Desorption (%)	5.8	4.5	3.3	2.9	3.5	3.1	2.3	4.2
	$D_d \times 10^8$ (cm^{2}s^{-1})	3.4	3.5	2.9	0.9	4.0	3.9	2.9	4.6
D	Sorption (%)	3.2	2.0	1.2	0.5	3.3	2.0	1.1	2.7
	Desorption (%)	5.4	3.6	3.0	2.8	4.5	3.4	2.4	3.2
	$D_d \times 10^8$ (cm^{2}s^{-1})	3.1	3.6	3.1	0.9	3.7	4.0	3.2	4.4
E	Sorption (%)	3.1	2.6	1.2	0.4	3.0	1.7	1.0	3.7
	Desorption (%)	5.0	4.4	3.1	2.8	4.0	2.9	2.4	4.2
	$D_d \times 10^8$ (cm^{2}s^{-1})	3.9	3.6	3.2	1.2	4.1	4.3	3.1	4.6

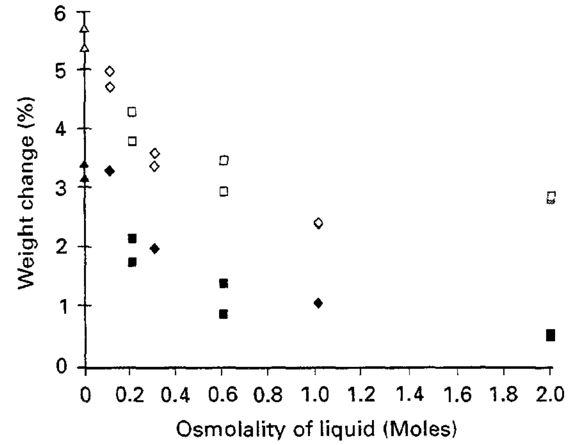

Figure 2 Water sorption for a typical experimental material as a function of the osmolality of immersing solution: ▲ water uptake; ■ NaCl uptake; ◆ glucose uptake; △ water desorption; □ NaCl desorption; ◇ glucose desorption.

4. Discussion

The formulations selected permit the isolation of the effects of various experimental factors by pairwise comparison of the results for selected materials and selected treatments. Comparing the DMA data for different formulations in Table II shows that both moduli and tan δ values are generally lower for the wet samples than the dry samples. This is interpreted as a result of the plasticizing effect of the water.

Changing the initiator from benzoyl (A and C) to lauryl peroxide (B and E) increased the dry modulus from 14.0 to 19.2 MPa and 19.9 to 20.9 MPa, respectively. However, the change had little effect on the other properties. Possibly the less reactive lauryl peroxide initiator may produce a higher molecular weight polymer.

Inclusion of the more hydrophobic monomer EHMA instead of HMA in B and D reduced the water uptake from 7.1 to 5.4%. A smaller decrease between the dry and wet moduli of the formulation D (2.9 MPa) relative to that of formulation B (7.6 MPa) is again perhaps due to the more hydrophobic character of EHMA.

In comparing the samples D and E, it was seen that increasing the content of the crosslinking agent (EGDM) from 0.5 to 1.0% resulted in an increase in the modulus. It also results in a decrease in water sorption from 5.4 to 5.0%. This is in accordance with the expectation that an increase in crosslink density will result in an increase in modulus and a decrease in water uptake. However, increasing the concentration of EGDM tends to increase water uptake because of increased oxygen content of the monomer [19]. It is a matter of speculation which one will predominate in a particular case. Here the crosslinking effect appears to be stronger.

The water sorption and the dynamic moduli of both wet and dry experimental materials exceeded those of Molloplast B and Super Soft (Table II). It was observed that tan δ for all experimental materials was within the range of the commercial material. The glass transition temperatures for all materials was below body temperature. The materials will feel hard to sudden loads but can adjust gradually to continuing force. Thus, they resemble Supersoft rather than Molloplast B. The water sorption data given in Table III shows that uptake from the sodium chloride and glucose solutions is lower than that from pure water.

With the exception of E, the water uptake of all materials from artificial saliva is also less than from pure water. However, the uptake from saliva is higher than from the other solutions in every case. Lowest uptake is from the saline solutions, this is to be expected if the process is osmotically driven as saline solutions of the same concentration will have higher osmotic pressures than non-ionizing glucose solutions.

The theory that the water uptake of methacrylate soft lining materials was osmotically driven was suggested by Parker and Braden [14]. They attributed the effect to the presence of water-soluble impurities giving rise to internal solution droplets, the driving force being the osmotic pressure gradient between the droplet and the external solution. Therefore, the higher the osmotic pressure of the solution the smaller the gradient, which results in lower uptake. Table III also shows relatively lower D_d values for highly concentrated solutions, especially 1 M sodium chloride and glucose than for pure water. This may be explained as due to build up of relatively higher viscosity at this concentration.

In Fig. 2 water uptake is plotted against the osmolality of saline and glucose solutions. The desorption plots differ from the sorption plots because the sorption data is decreased by the leaching out of soluble matter. However, it is clear that saline and glucose solution data superimpose when the osmolality of the solutions is considered. This supports the hypothesis that the driving force is osmotic, and strictly speaking the chemical potential gradient, as originally shown by Muniandy and Thomas [20].

5. Conclusions

(i) Increasing the crosslinking agent (0.5 to 1.0% EGDM) in systems D and E resulted in an increase in modulus and a decrease in water sorption.

(ii) Changing initiator from benzoyl to lauryl peroxide in formulations A, B and C, E, increased dry modulus but had little effect on other properties.

(iii) Inclusion of EHMA instead of HMA (formulations B, D) reduced water uptake (7.1 to 5.4%) and dry modulus (19.2 to 15.9 MPa) and reduced the decrease in modulus caused by water sorption (from 7.6 MPa to 2.9 MPa). Tan δ values for all experimental materials lie within the range of accepted commercial materials. Dynamic moduli both wet and dry and water sorption generally exceeded those of the commercial materials studied.

(iv) Water uptake measurements of all the experimental materials in saline and glucose solutions of various concentrations at 37 °C, confirmed that the diffusion process is osmotically driven, i.e. the chemical potential gradient is the driving force.

Acknowledgements

This research was supported by grant number DE 09425 from the National Institute of Dental Research. The authors wish to thank Dr Sankar Pandian for assisting with some DMA and water sorption measurements.

References

1. J. B. GONZALES and W. R. LANEY, *J. Prosthet. Dent.* **16** (1966) 438.
2. E. A. TRAVAGLINI, P. GIBBONS and R. G. CRAIG, *ibid.* **10** (1960) 664.
3. R. TODD and J. A. HOLT, *ibid.* **51** (1987) 247.
4. E. D. ADRIAN, W. A. DRANTZ and J. R. IVANHOE, *ibid.* **67** (1992) 212.
5. P. S. WRIGHT, *J. Dent.* **4** (1976) 247.
6. M. BRADEN and P. S. WRIGHT, *J. Dent. Res.* **62** (1983) 764.
7. S. PARKER and M. BRADEN, *J. Dent.* **10** (1982) 149.
8. P. S. WRIGHT, *ibid.* **9** (1981) 210.
9. M. BRADEN and R. L. CLARKE, *J. Dent. Res.* **51** (1972) 1525.
10. P. S. WRIGHT, *ibid.* **61** (1982) 1002.
11. E. R. DOOTZ, A. KORAN and R. G. CRAIG, *J. Prosthet. Dent.* **67** (1992) 707.
12. P. S. WRIGHT, *J. Dent.* **8** (1980) 144.
13. *Idem.*, *J. Dent. Res.* **59** (1980) 614.
14. S. PARKER and M. BRADEN, *Biomaterials* **10** (1989) 91.
15. S. KALACHANDRA; R. J. MINTON, T. TAKAMATA and D. F. TAYLOR, *J. Mater. Sci. Mater. Med.* **6** (1995) 218.
16. S. KALACHANDRA and D. T. TURNER, *Polymer* **28** (1987) 1749.
17. S. KALACHANDRA and D. T. TURNER, *Dent. Mater.* **5** (1989) 161.
18. S. KALACHANDRA and D. T. TURNER, *J. Biomedical Mater. Res.* **21** (1987) 329.
19. S. KALACHANDRA and P. P. KUSY, *Polymer* **32** (1991) 2428.
20. K. MUNIANDY and A. G. THOMAS, "Polymers in marine environment" (*Inst. Marine Engineers, London* (c), 1984) 97, Conf. 2 Paper 13.

Received 22 June
and accepted 7 September 1995