

Dynamic viscoelastic properties of antimicrobial tissue conditioners containing silver–zeolite[☆]

M. Ueshige, Y. Abe^{*}, Y. Sato, K. Tsuga, Y. Akagawa, M. Ishii

Department of Removable Prosthodontics, Hiroshima University School of Dentistry, Kasumi 1-2-3, Minami-ku, Hiroshima 734-8553, Japan

Received 27 July 1998; received in revised form 23 November 1998; accepted 13 January 1999

Abstract

Objectives: The purpose of this study was to determine the effects of including the antimicrobial silver–zeolite (SZ) on the dynamic viscoelastic properties of various tissue conditioners.

Methods: The dynamic viscoelastic properties of five commercially available tissue conditioners: Visco-gel (VG), GC Soft-Liner (SL), FITT (FT), SR-Ivoseal (IV) and Shofu Tissue Conditioner (TC) containing SZ were evaluated after 1 and 28 days of water- and artificial saliva immersions with the use of complex modulus and loss tangent parameters. Values for these two parameters for each tissue conditioner were statistically analyzed by one- and two-way ANOVA and Bonferroni's test.

Results: Complex modulus and loss tangent values of TC were not significantly different among specimens containing 0, 2, 5 and 10 wt.%-SZ, respectively. In FT and TC containing 2 wt.%-SZ, these values were not significantly different between 1 and 28 days in both water- and saliva immersions.

Conclusion: The results suggest that incorporating SZ does not affect TC's inherent dynamic viscoelastic properties, while the other tissue conditioners investigated may be found to have changed viscoelastic properties as a consequence of the inclusion of SZ. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Tissue conditioner; Antimicrobials; Silver–zeolite; Viscoelasticity

1. Introduction

It is important to realize in the clinical use of tissue conditioners that these materials are readily degradable and susceptible to colonization by micro-organisms [1]. Unless a tissue conditioner is replaced regularly, it acts as a reservoir for micro-organisms and can cause complications. In elderly patients who have decreased immunological activity, such complications, including pharyngeal and respiratory tract problems [2,3], are inevitable when microorganisms have accumulated on tissue conditioners. For example, *Staphylococcus aureus*, giving rise to respiratory infections, has been isolated from dentures and the oral cavity [4–6]. Therefore, the maintenance of tissue conditioners and the prevention of the accumulation of micro-organisms on such materials are important. For the

maintenance of tissue conditioners, it is thought that mechanical and chemical cleaning methods are sufficient. However, it is also known that these methods can cause considerable damage to tissue conditioners [7]. Another approach is the use of nystatin, miconazole or ketoconazole [8–10]. However, little information is available on the merits of this approach [11,12].

Silver–zeolite (SZ) has been shown to possess long-term antimicrobial effects against almost all microbes [13], given the continuous release of small amounts (ca. 10 ppb) of silver ions (Ag^+) from SZ into water [14]. Favorable in vitro, 28-day antimicrobial effects of tissue conditioners containing SZ on *Candida albicans* and nosocomial respiratory infection-causing bacteria, *Staphylococcus aureus* and *Pseudomonas aeruginosa* have been previously reported [15]. These results lend support to the incorporation of SZ in tissue conditioners. However, a question arises as to whether incorporating SZ in tissue conditioners may change the mechanical properties of these materials. The viscoelastic properties of tissue conditioners are important to the clinical performance and success of these materials. No information is available on the viscoelastic properties of tissue conditioners containing an antimicrobial agent.

[☆] This study was supported by a Grant-in-Aid for Developmental Scientific Research (B) (No.07557273) from the Ministry of Education, Science, Sports and Culture, Japan (1995). A part of this study was presented at 7th Meeting of the International College of Prosthodontists in Malta, 1997.

^{*} Corresponding author. Tel.: +81-82-257-5677; fax: +81-82-257-5679.

E-mail address: abey@ipc.hiroshima-u.ac.jp (Y. Abe)

Table 1
Tissue conditioners

Brand name	Manufacturer	Batch	Code
Visco-gel	De Trey/Dentsply, Weybridge, UK	PK43	VG
GC Soft-Liner	GC Co., Tokyo, Japan	271051	SL
FITT	Kerr, Romulus, MI, USA	3-1231	FT
SR-Ivoseal	Ivoclar–Vivadent, Lichtenstein	616330	IV
Shofu Tissue Conditioner	Shofu Inc., Kyoto, Japan	109565	TC

This study was, therefore, designed to determine the influence of SZ on the dynamic viscoelastic properties of five commercially available tissue conditioners.

2. Materials and methods

2.1. Tissue conditioners

Five commercially available tissue conditioners; Visco-gel (VG), GC Soft-Liner (SL), FITT (FT), SR-Ivoseal (IV) and Shofu Tissue Conditioner (TC) were selected for investigation (Table 1).

2.2. Specimen preparation

SZ (Zeomic® AJ10N, Shinagawa Fuel Co., Nagoya, Japan) (Table 2 and Fig. 1) was first incorporated (0, 2, 5 and 10% by dry wt.) into the powder of each tissue conditioner, and then mixed with the respective liquid according to the manufacturer's instructions. The mixed material was put on a glass plate (150 × 70 × 10 mm) with a 5 mm-thickness metal frame spacer and then covered for 3 h with a second glass plate. The set material was then cut into pieces of 10 × 10 × 5 mm. Specimens containing 0 wt.-%-SZ were used as controls. In total, 20 specimens were prepared for each of the incorporations. Ten specimens were randomly selected and immersed in distilled water. The remaining 10 specimens were immersed in

Table 2
The properties of silver–zeolite (Zeomic® AJ10N)

Structural formula	$\text{MX}_{2/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{YSiO}_2 \cdot \text{ZH}_2\text{O}$ M: Cation (Ag^+ , Zn^{2+} and other cations) X, Y and Z: Mole fraction of each component
Weight percentage of components	Ag^+ : 2.5 wt.%; Zn^{2+} : 14.5 wt.%; NH_4^+ : 2.5 wt.%; H_2O : 16 ~ 18 wt.%
Shape	White powder
Porus size	0.4 nm
Specific gravity	2.1
Average particle size	0.6 ~ 2.5 μm
Specific heat	0.26 cal/g
Heat resistance	550°C
Acidity resistance	pH 3
Alkalinity resistance	pH 10

artificial saliva prepared in a thermostat at 37°C by the S-Gravenmade method [16].

2.3. Measurements of dynamic viscoelastic properties

The dynamic viscoelastic properties of five specimens of each tissue conditioner following water and artificial saliva were measured at 1 and 28 days using an automatic dynamic viscoelastometer (RHEOVIBRON DDV-25FP, Orientec Inc., Tokyo, Japan). Specimens were set in a compression jig and tested at a frequency of 1 Hz and a temperature of 37°C. The ratio of amplitude and phase difference between applied sinusoidal strain and resulting stress through the specimen were measured by a non-resonance forced vibration method. The complex modulus (E^*) was then calculated by the expression: $\{\text{storage modulus } (E')^2 + \text{loss modulus } (E'')^2\}^{1/2}$. Loss tangent ($\tan \delta$) was calculated by the equation: E'/E'' . E' describes the elastic stiffness of the material and E'' describes the viscous behavior, and high E^* may generally indicate a characteristic of being hard to deform. $\tan \delta$ means the scale of energy loss, and materials that absorb energy as a result of deformation show a high $\tan \delta$ value.

2.4. Statistical analysis

One- and two-way ANOVA and Bonferroni's test for multiple comparisons were used to statistically analyze the mean values of E^* and $\tan \delta$ for the degrees of SZ incorporation under each immersion condition and period at a 0.01 probability level.

3. Results

Changes of E^* and $\tan \delta$ values for each tissue conditioner containing SZ at 1 day of immersion are shown in Fig. 2(a) and (b). The E^* values of SL decreased significantly with increasing SZ content, while $\tan \delta$ values of FT and IV increased. The $\tan \delta$ value of VG containing 10 wt.-%-SZ was lower than for the control. Only with TC, were E^* and $\tan \delta$ values unchanged by degrees of SZ incorporation.

Longitudinal changes of E^* and $\tan \delta$ values for each tissue conditioner containing 2 wt.-%-SZ under each immersion are shown in Figs. 3 and 4. In water immersion (Fig. 3), while E^* values at 28 days for control VG and SL showed

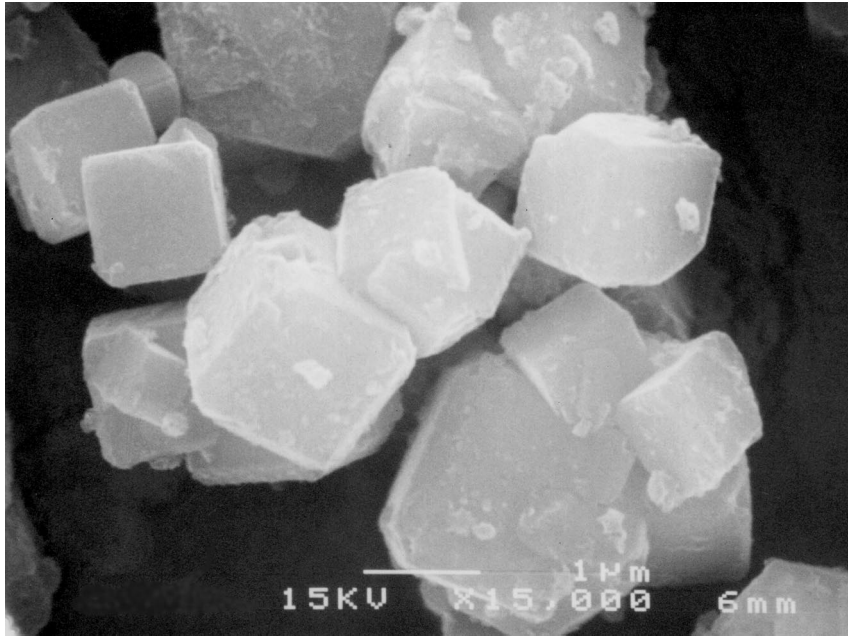


Fig. 1. SEM of Zeomic AJ10N. Bar scale:1 μm.

almost the same changes compared with E^* values at 1 day, SL containing 2 wt.%-SZ had increased and VG containing 2 wt.%-SZ had decreased. In saliva immersion (Fig. 4), E^* values at 28 days for all tissue conditioners containing

2 wt.%-SZ showed almost the same changes compared with E^* values at 1 day, unlike the E^* value of control IV. In both water- and saliva immersion, E^* and $\tan \delta$ values at 28 days for FT and TC containing 2 wt.%-SZ showed almost the same changes compared with E^* and $\tan \delta$ values at 1 day.

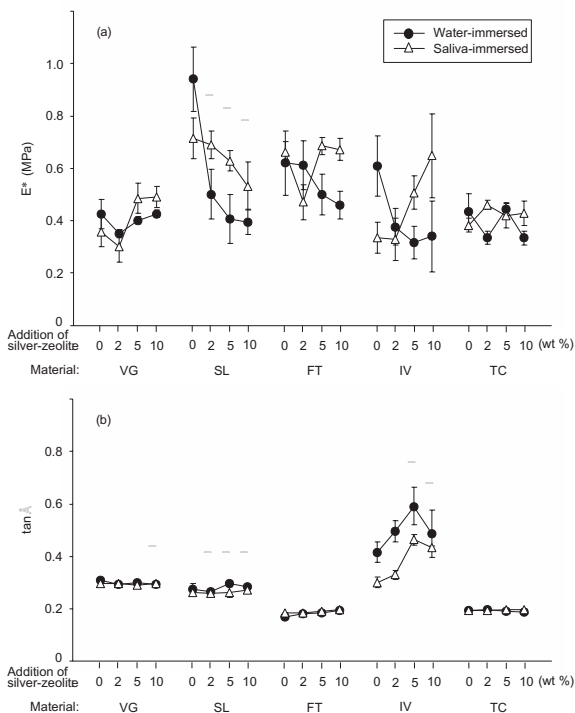


Fig. 2. Mean E^* and $\tan \delta$ values for five tissue conditioners containing silver-zeolite at 1 day. *: significant difference compared with control ($p < 0.01$). VG: Visco-gel, SL: GC Soft-Liner, FT: FITT, IV: SR-Ivoseal, TC: Shofu Tissue Conditioner.

4. Discussion

The findings of this study indicate that the addition of SZ does not affect dynamic viscoelastic properties of TC, while other tissue conditioners were affected.

The mechanical properties of tissue conditioners are important because they can influence the success of the material's functions. For measurements of the mechanical properties of tissue conditioners, two methods are most generally available, one is static [17] and the other is dynamic viscoelastic testing [18–20]. The latter testing characterizes the periodic deformation of tissue conditioners which occurs in clinical use. This testing, which is commonly used in the study of polymeric material development, subjects the material to various frequencies and temperatures and evaluates the effects of these conditions. In this study, dynamic viscoelastic testing was conducted at a frequency of 1 Hz and a temperature of 37°C, because these conditions closely approximate the oral environment [21].

The viscoelastic properties of tissue conditioners vary among materials because of the differences in chemical composition and structure (e.g. molecular weight of plasticizer and polymer, ethanol content, and the Polymer/Liquid ratio) [22–24]. When SZ is included in a tissue conditioner, it is probable that SZ influences the structure of the

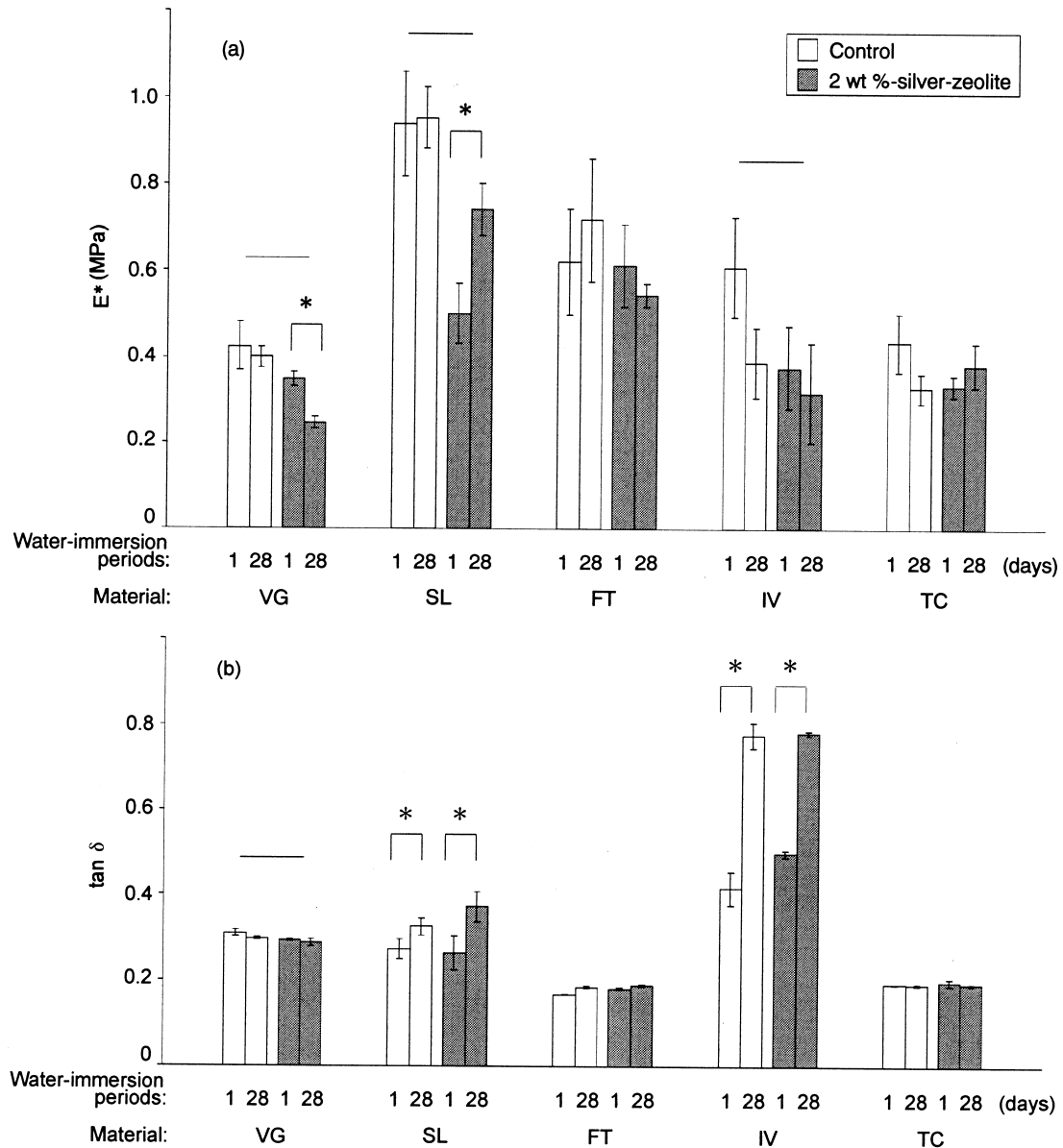


Fig. 3. Mean E^* and $\tan \delta$ values for five tissue conditioners containing 2 wt.%-silver-zeolite and control at 1 and 28 days in water-immersion. *: significant difference between 1 and 28 days values ($p < 0.01$). Horizontal bars indicate significant differences between specimens containing 2 wt.% silver-zeolite and control. VG: Visco-gel, SL: GC Soft-Liner, FT: FITT, IV: SR-Ivoseal, TC: Shofu Tissue Conditioner.

conditioner. In the initial mixing of the powder and liquid of the material, the ethanol is absorbed into polymer particles and this absorption makes the powder particles swell. Polymer chains disentanglements then occurs. These disentanglements allow the higher molecules of the plasticizers to penetrate between polymer chains. Eventually, homogeneity with the polymer chains contained in ethanol and the plasticizer is achieved and gel formation is displayed [25]. SZ possibly influences the penetration of plasticizers, and as a result, the inherent dynamic viscoelastic properties of the materials are presumed to be changed. However, the magnitude of the influences differed among the materials used in this study and this may be explained by the different

molecular weight of the plasticizers. It is known about plasticizers that butyl phthalyl butyl glycolate (BPBG) (mol. wt. 336) is mainly contained in VG and SL, dibutyl phthalate (DBP) (mol. wt. 278) in FT and TC, and dibutyl sebacate (DBS) (mol. wt. 314) in IV. BPBG with a higher molecular weight slowly penetrates into polymer chains, and after penetration, it produces stronger gel formation [22]. SZ may hinder BPBG from penetrating and weaken gel formation, as the E^* value of SL containing SZ decreased compared with that of the control (Fig. 2). In contrast, the E^* value of VG containing BPBG was not influenced by the incorporation of SZ. The difference in the behavior between VG and SL could be due to the

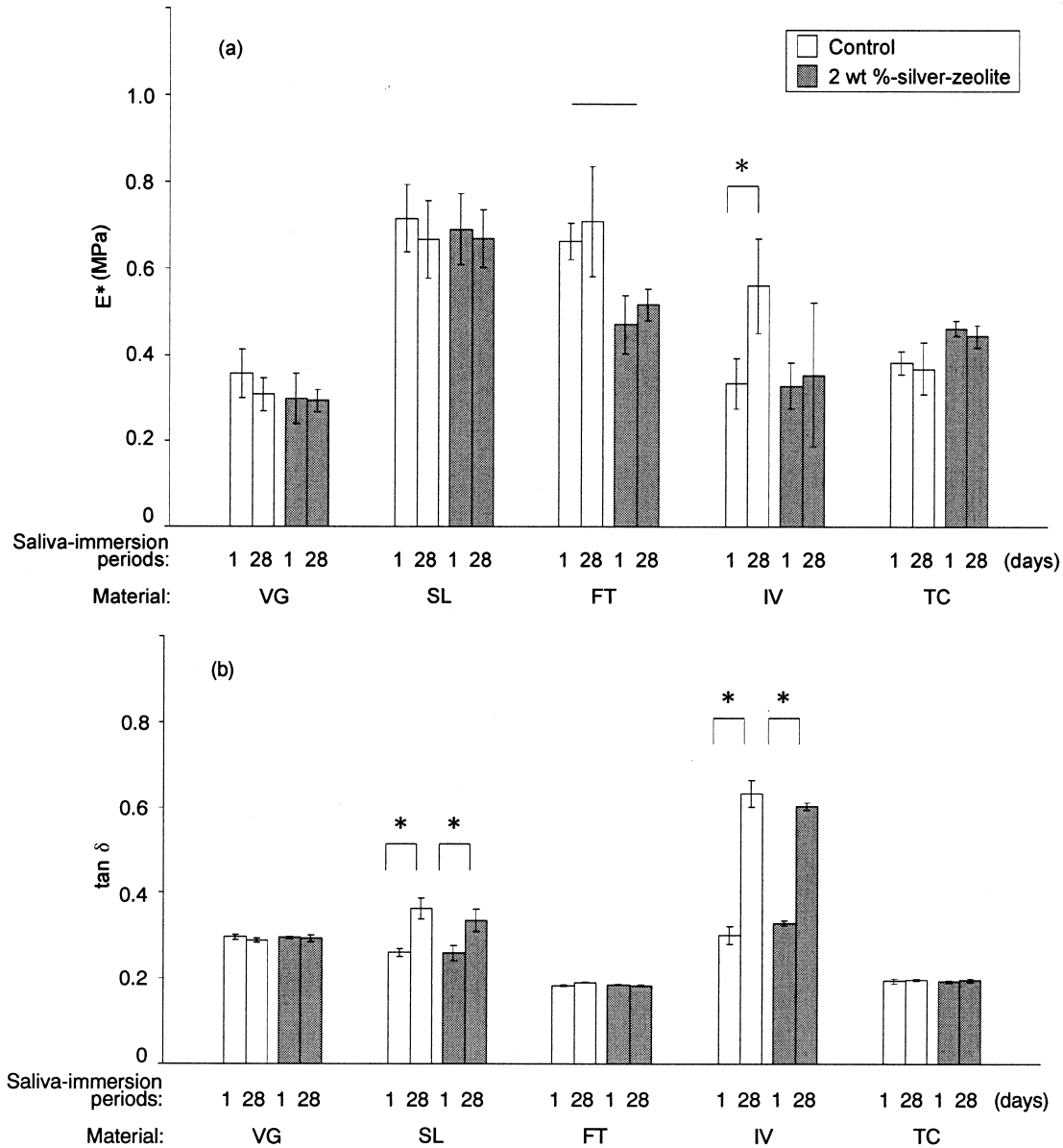


Fig. 4. Mean E^* and $\tan \delta$ values for five tissue conditioners containing 2 wt.% silver-zeolite and control at 1 and 28 days in saliva-immersion. *: significant difference between 1 and 28 days values ($p < 0.01$). Horizontal bars indicate significant differences between specimens containing 2 wt.%-silver-zeolite and control. VG: Visco-gel, SL: GC Soft-Liner, FT: FITT, IV: SR-Ivoseal, TC: Shofu Tissue Conditioner.

difference of the molecular weight of the polymer. Higher molecular weight polymers will take longer to swell, diffuse and dissolve [25]. The molecular weights of VG polymer (179 000) are lower than those of SL (234 000) [23] and may be easily penetrated by plasticizers, with the result that the E^* value of VG was not changed despite containing SZ.

In the longitudinal changes, the E^* values of water-immersed VG, SL and IV, and saliva-immersed FT containing 2 wt.%-SZ decreased significantly compared with those of the control (Figs. 3 and 4). As mentioned earlier, the molecular weights of the plasticizer and the polymer may induce these changes in VG and SL. With regard to IV and FT, the change in the viscoelastic properties of these

materials over time possibly resulted from the leaching out of ethanol. Ethanol diffuses out easily due to the low molecular weight, resulting in a great loss from tissue conditioners, and influence on their viscoelastic properties over time of storage [24]. It is known that concentrations of ethanol in IV (48.1%) and FT (19.6%) are higher than those in VG (4.9%), SL (14.8%) [26], and TC (15.0%). Owing to the lower molecular weight of the plasticizer and comparatively lower concentration of ethanol, the viscoelastic properties of TC containing SZ might hardly be changed.

On the basis of this limited study, TC containing SZ is a possible candidate for a novel antimicrobial tissue

conditioner. However, for clinical application, the discoloration of TC containing SZ and the effect on the composition of oral microflora should be evaluated.

Acknowledgements

Silver–zeolite (Zeomic® AJ10N) was supplied by Shinagawa Fuel Co., Nagoya, Japan.

References

- [1] Okita N, Ørstavik D, Ørstavik J, Østby K. In vivo and in vitro studies on soft denture materials: microbial adhesion and tests for antibacterial activity. *Dental Materials* 1991;7:155–160.
- [2] Johanson Jr. WG, Pierce AK, Sanford JP, Thomas GD. Nosocomial respiratory infections with gram-negative bacilli. The significance of colonization of the respiratory tract. *Annals of Internal Medicine* 1972;77:701–706.
- [3] Mbaki N, Rikitomi N, Nagatake T, Matsumoto K. Correlation between *Branhamella catarrhalis* adherence to oropharyngeal cells and seasonal incidence of lower respiratory tract infections. *Tohoku Journal of Experimental Medicine* 1987;153:111–121.
- [4] Wilkieson C, Samaranyake LP, MacFarlane TW, Lamey P-J, MacKenzie D. Oral candidosis in the elderly in long term hospital care. *Journal of Oral Pathology and Medicine* 1991;20:13–16.
- [5] Marsh PD, Percival RS, Challacombe SJ. The influence of denture-wearing and age on the oral microflora. *Journal of Dental Research* 1992;71:1374–1381.
- [6] Rossi T, Laine J, Eerola E, Kotilainen P, Peltonen R. Denture carriage of methicillin-resistant *Staphylococcus aureus*. *Lancet* 1995;345:1557.
- [7] Harrison A, Basker RM, Smith IS. The compatibility of temporary soft materials with immersion denture cleansers. *International Journal of Prosthodontics* 1989;2:254–258.
- [8] Truhlar MR, Shay K, Sohnle P. Use of a new assay technique for quantification of antifungal activity of nystatin incorporated in denture liners. *Journal of Prosthetic Dentistry* 1994;71:517–524.
- [9] Quinn DM. The effectiveness, in vitro, of miconazole and ketoconazole combined with tissue conditioners in inhibiting the growth of *Candida albicans*. *Journal of Oral Rehabilitation* 1985;12:177–182.
- [10] Carter GM, Kerr MA, Shepherd MG. The rational management of oral candidosis associated with dentures. *New Zealand Dental Journal* 1986;82:81–84.
- [11] Budtz-Jørgensen E, Theilade E, Theilade J, Zander HA. Method for studying the development structure and microflora of denture plaque. *Scandinavian Journal of Dental Research* 1981;89:149–156.
- [12] Koopmans ASF, Kippuw N, de Graaff J. Bacterial involvement in denture-induced stomatitis. *Journal of Dental Research* 1988;67:1246–1250.
- [13] Uchida T, Maru N, Furuhashi M. Anti-bacterial zeolite balloon catheter and its potential for urinary tract infection control. *Acta Urologica Japonica* 1992;38:973–978.
- [14] Breck DW. Ion exchange reactions in zeolites. In *Zeolite Molecular Sieves: Structure Chemistry and Use Chapter 7*. New York: Wiley, 1974 529–592.
- [15] Matsuura T, Abe Y, Sato Y, Okamoto K, Ueshige M, Akagawa Y. Prolonged antimicrobial effect of tissue conditioners containing silver–zeolite. *Journal of Dentistry* 1997;25:373–377.
- [16] 'S-Gravenmade EJ. Artificial saliva. *International Journal of Oral Surgery* 1974;3:435–439.
- [17] Kawano F, Tada N, Nagao K, Matsumoto N. The influence of soft lining materials on pressure distribution. *Journal of Prosthetic Dentistry* 1991;65:567–575.
- [18] Duran RL, Powers JM, Craig RG. Viscoelastic and dynamic properties of soft liners and tissue conditioners. *Journal of Dental Research* 1979;58:1801–1807.
- [19] Wagner WC, Kawano F, Dootz ER, Koran III A. Dynamic viscoelastic properties of processed soft denture liners: Part I—initial properties. *Journal of Prosthetic Dentistry* 1995;73:471–477.
- [20] Wagner WC, Kawano F, Dootz ER, Koran III A. Dynamic viscoelastic properties of processed soft denture liners: Part II—effect of aging. *Journal of Prosthetic Dentistry* 1995;74:299–304.
- [21] Lundeen HC, Gibbs CH. *Advances in occlusion*. Boston, MA: Jhon Wright, 1982.
- [22] Jones DW, Sutow EJ, Graham BS, Milne EL, Johnston DE. Influence of plasticizer on soft polymer gelation. *Journal of Dental Research* 1986;65:634–642.
- [23] Jones DW, Hall GC, Sutow EJ, Langman MF, Robertson KN. Chemical and molecular weight analyses of prosthodontic soft polymers. *Journal of Dental Research* 1991;70:874–879.
- [24] Murata H, Murakami S, Shigeto N, Hamada T. Viscoelastic properties of tissue conditioners — influence of ethyl alcohol content and type of plasticizer. *Journal of Oral Rehabilitation* 1994;21:145–156.
- [25] McCarthy JA, Moser JB. Tissue conditioning and functional impression materials and techniques. *Dental Clinics of North America* 1984;28:239–251.
- [26] Jones DW, Sutow EJ, Hall GC, Tobin WM, Graham BS. Dental soft polymers: plasticizer composition and leachability. *Dental Materials* 1988;4:1–7.