Relaxation Modulus of Denture Base Resin Reinforced with Woven Glass Fibers

Takahito KANIE, Hiroyuki ARIKAWA and Koichi FUJII

Department of Biomaterials Science, Kagoshima University Dental School
8-35-1 Sakuragaoka, Kagoshima 890-8544, Japan

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This study examined the reinforcing effect of woven glass fibers on the relaxation modulus by three-point loading of denture base resin. Three sandwich-type flexure test specimens polymerized by heating were used, all 3 mm thick: glass fibers in compression (U type); glass fibers in the center (C type); and glass fibers in tension (L type). Unreinforced specimens (ACR) were produced as a control. The relaxation modulus after 8 sec from the start of stress $|Er(8)|$ was calculated from stress relaxation curves. In the glassy state, the $Er(8)s$ of the U and L types were greater than those of the ACR and C types. In the rubbery state (plateau region), the $Er(8)s$ of the U and L types were greater than those of the ACR and C types. The woven glass fibers added to the U and L type specimens increased the relaxation modulus of PMMA near the oral temperature; moreover, they inhibited stress relaxation when the temperature increased.

Key words : Denture base resin, Woven glass fiber, Relaxation modulus

INTRODUCTION

Polymethylmethacrylate (PMMA) is commonly used as a denture base resin because of its excellent manipulation and aesthetic properties. However, this material has some disadvantages, such as its low resistance to fractures caused by impact or repeated loading. Many studies have examined methods of reinforcing denture base resins to improve their mechanical strength, and one such method involves the use of glass fibers¹⁻⁶⁾.

When glass fibers are added to resin dough, they are typically inserted by hand. Consequently, the position of the glass fibers in the dough is inconsistent, because the thickness of the dough with respect to the denture base resin thickness is not uniform. Some studies⁷⁻⁹⁾ have examined the relationship between flexural strength and the location or direction of the glass fibers. However, it is not clear from these studies whether the attempted reinforcement is effective in improving the mechanical properties of the denture base resin, since, with few exceptions, they have discussed only breaking load. Moreover, there are few reports on the properties of reinforced denture base resin in the elastic deformation region, before it breaks.

Moreover, an amorphous polymer, such as denture base resin, responds as an elastic body when deformed at a high frequency, whereas it acts as a viscoelastic body when deformed at a low frequency. Thus, the mechanical properties of a polymer can vary with changes in the deformation time scale, as well as with changes in

temperature¹⁰⁻¹²). Therefore, it is important to examine the viscoelastic property of reinforced denture base resin within proportional limits in the oral temperature range.

This study measured the change in the relaxation modulus with temperature of denture base resin reinforced with two woven glass fibers, and discusses the materials' viscoelastic properties.

MATERIALS AND METHODS

Acrylic resin (Acron, GC Corp., Tokyo, Japan) was used as the denture base resin in this investigation. Powder and liquid were mixed in a ratio of 100 g/43 ml to form a dough. Details of the two E-glass fibers (Codes, P and S), containing 52-56 wt% SiO₂, 12-16 wt% Al₂O₃, 16-25 wt% CaO, and 5-13 wt% B₂O₃ according to the manufacturer's specifications (Mie Textile Co. Ltd., Tsu, Japan), are given in Table 1 and Fig. 1.

γ -Methacryloxypropyltrimethoxysilane (γ -MPS) (Dow Corning Toray Silicone Co. Ltd., Tokyo, Japan) was used as a silane-coupling agent. The glass fibers were cleaned in boiling water for 10 min and dried in air, then soaked for 1 min with undiluted γ -MPS, dried in air for 1 hr, and placed in an oven for 6 hr at 115°C.

The dough was pressed at 2 MPa into a Teflon mold and shaped into a sheet (80 mm long and 40 mm wide). The sheets were 1.0, 1.5, or 2.0 mm thick. The composite, incorporating the silanized glass fibers between two sheets (either two 1.5 mm-thick sheets or one 1.0 and one 2.0 mm-thick sheet), was put into a 3 mm-deep Teflon

Table 1 Physical properties of the two woven glass fibers used in this investigation

Code	Trade name	Texture	Standard thickness (mm)	Tensile strength (N/25 mm)	Density (threads/25 mm)	
				Longitudinal	Warp	Weft
P	YCTM13075	Plain fabric	0.13	382	19	19
S	YEA1801	Satin elastic webbing	0.16	1451	46	25

Fig. 1 Two E-glass fibers (Codes, P and S) and their textures illustrated by the manufacturer.

mold. The mold was then pressed at 2 MPa and the dough impregnated into the woven glass fibers. Three sandwich-type test specimens were used, all 3 mm thick: U and L types {polymer (1 mm)+glass fiber+polymer (2 mm)}; and C type {polymer (1.5 mm)+glass fiber+polymer (1.5 mm)} (Fig. 2). The curing process consisted of heating for 1 hr at 70°C, followed by 1 hr at 100°C under a N₂-gas pressure of 0.5 MPa. The cured composite was cut into rectangular pieces using a cutting machine with a water-cooled diamond blade, and then the test specimens were polished with Emery paper (#320) 7 mm wide, 3 mm thick, and 22 mm long. Unreinforced specimens (ACR) were produced as a control. The test specimens were stored in an air cabinet at 37±1°C for 2 weeks.

The relaxation modulus was measured by means of three-point flexure, using a

Code	Group	Test specimen
ACR	Control	= 3.0 mm
P-U	U type	= 1.0/2.0 mm
S-U		
P-C	C type	= 1.5/1.5 mm
S-C		
P-L	L type	= 2.0/1.0 mm
S-L

Fig. 2 Classification of test specimens incorporating woven glass fibers.

Fig. 3 Schematic representation to determine the apparent glass transition temperature (T_g) from the relaxation modulus-temperature curve.

stress relaxation-testing device (Thrive Seiko Ltd., Kagoshima, Japan)¹²⁾ with a span length of 15 mm. In this study, three measurements for each material were made, using a constant flexural strain within 0.4% under the proportional limit. The $Er(8)$ -temperature curves were plotted using the median of the three obtained values. From the $Er(8)$ -temperature curves, the $Er(8)$ at 20, 37, and 60°C for oral thermal change and the apparent glass transition temperature (T_g) were determined (Fig. 3)¹³⁾. The temperature was increased from 20 to 140°C at a heating rate of 0.5°C/min.

The relaxation modulus $\{Er(8)\}$ was calculated using the formula:

$$Er(8) = \frac{P(8)l^3}{4bh^3d}$$

where d is the deflection corresponding to the load $P(8)$, which is the load after 8 sec from the start of stress. l , b , and h are the span length, width, and thickness of the test specimens, respectively.

The data were analyzed using one-way ANOVA, two-way ANOVA and Tukey's test (5% significance level).

RESULTS

The variation in the relaxation modulus $\{Er(8)\}$ with temperature is shown in Figs. 4 and 5. At temperatures below T_g (glassy state), the $Er(8)$ values of the U (P-U and S-U) and L (P-L and S-L) types were larger than those of the ACR and C types

Fig. 4 Variations of relaxation modulus, $Er(8)$ with temperature of ACR, P-C, P-U and P-L.

Fig. 5 Variations of relaxation modulus, $Er(8)$ with temperature of ACR, S-C, S-U and S-L.

Table 2 $Er(8)$ at 20°C, at 37°C and at 60°C and T_g

Code	$Er(8)$ at 37°C (GPa)	$Er(8)$ at 20°C (GPa)	$Er(8)$ at 60°C (GPa)	T_g (°C)
ACR	1.45 (0.01)	1.48 (0.01)	1.22 (0.01)	103.1 (0.4)
P-C	1.21 (0.02)	1.25 (0.02)	1.11 (0.02)	106.6 (0.3)
P-U	1.77 (0.01)	1.79 (0.03)	1.71 (0.02)	107.8 (0.5)
P-L	1.57 (0.03)	1.62 (0.02)	1.47 (0.03)	107.9 (0.4)
S-C	1.37 (0.01)	1.39 (0.02)	1.31 (0.02)	107.7 (0.6)
S-U	2.20 (0.02)	2.16 (0.01)	2.06 (0.02)	109.1 (0.6)
S-L	1.88 (0.01)	1.91 (0.02)	1.87 (0.01)	109.1 (0.4)

(): Standard deviation

(P-C and S-C). In the rubbery state (plateau region), which is at a higher temperature range than the glass transition region, the $Er(8)$ s of the U and L types were larger than those of the ACR and C types.

The $Er(8)(37^\circ\text{C})$, $Er(8)(20^\circ\text{C})$, $Er(8)(60^\circ\text{C})$, and T_g are shown in Table 2. The differences in the values of $Er(8)(37^\circ\text{C})$ for all types of test specimens examined were statistically significant ($p < 0.05$). For P-U, P-L, and S-L types, there was no statistical difference ($p > 0.05$) in the $Er(8)$ s between 20°C and 60°C ; therefore, P-U, P-L and S-L types are stable for oral thermal change. The difference in $Er(8)$ between 20°C and 60°C in ACR was the largest of all the test specimens. The T_g of all the test specimens reinforced with woven glass fibers was higher than that of ACR ($p < 0.05$).

Table 3 Results of two-way ANOVA of Er(8) at 37°C

Source	s.s	d.f	m.s	F
Incorporating portion: (A)	1.4789	2	0.7394	3.8853*
Fiber quantity: (B)	0.4043	1	0.4043	4.7472*
Interaction: (A×B)	0.0559	2	0.0280	3.8853*
Error	0.0031	12	0.0003	
Total	1.9423	17		

*P<0.05

Table 3 shows the results of two-way ANOVA for the Er(8)(37°C). Incorporating the portion, fiber quantity and interaction effect significantly influenced the Er(8)(37°C) ($p<0.05$).

DISCUSSION

In general, the mechanical properties of denture base resin are estimated using the three-point flexural test, because the base of dentures bends with biting. In the three-point flexural test, the top surface of the test specimen at the point of the applied load is placed in a state of compression, whereas the bottom surface is under tension. It is known that, in the flexural test, fractures progress from the bottom surface to the neutral plane, because the stress concentrated in the bottom surface under tension is apt to generate micro-cracks that gradually propagate inward¹⁴⁻¹⁶. Therefore, it is important to increase the resistance of denture base resins against fracture, to inhibit the formation of micro-cracks. Previous investigations^{7,8} in which the flexural strength and modulus were measured using different amounts of reinforcing materials reported no significant difference between test specimens reinforced in the upper (U type), middle (C type), or lower (L type) portions. On the other hand, in this investigation, the relaxation moduli of U and L type specimens over the entire temperature range from 20-140°C were larger than those of C type specimens. These results indicate that the difference arises from viscoelastic properties that are not quantified in breaking tests such as compressive or tensile tests using a universal testing machine. For the L type, as mentioned by a previous report⁹, it appears that the woven glass fibers, which are superior to polymers in tensile strength, inhibited the deformation.

The relaxation modulus is an important property to consider, as denture base resins are subjected to continuous stress or strain during occlusion. The Er(8) value tentatively quantifies the flow of materials. In other words, materials with a low Er(8) are easy to deform, because the molecules slip past one another. Comparing the Er(8) values at the temperature of the oral cavity (37°C), the addition of reinforcing materials distinctly increased the relaxation modulus in U and L type specimens, but not in C-type specimens. Consequently, denture base resin that is reinforced in the upper or lower positions (U or L types) is not easily deformed by stress caused during occlusion in the oral cavity, and reinforcement in the upper

position (U type) is particularly effective. These results imply that the rigidity of woven glass fibers used as a reinforcing material inhibits the flow of denture base resin when subjected to tensile or compressive stresses. However, there was no significant difference between the Er(8)s of the C type and ACR at 37°C. This might have been primarily because the woven glass fibers were placed in the neutral plane; the position of insertion of the woven glass fibers had a direct effect on the flexural modulus of the denture base resin.

In the glassy state, the relaxation modulus tended to decrease when the temperature increased from 20 to 60°C. This phenomenon likely occurs because slippage between molecular chains occurs easily with increasing specific volume. The ratio of the Er(8) values at 20°C and 60°C was smaller for ACR (0.82) than for the reinforced materials (Table 2), which ranged from 0.89 to 1. The Er(8)s of the reinforced materials dropped only slightly with increasing temperature, compared with ACR. This suggests that a denture base resin containing a woven glass fiber is minimally deformed by changing temperature in the oral cavity.

Although the Er(8) values of all the materials examined showed a marked decline with increasing temperature, in the transition region, the Er(8) values of the materials reinforced with woven glass fibers were larger than that of ACR, and, moreover, their Tgs increased. The drop in Er(8) values can be explained by the commencement of micro-Brownian motion, in which a segment of the main molecular chain is emancipated from the frozen state in the glassy region. In addition, these results suggest that the woven glass fibers added to PMMA play an important role as a cross-linking agent. Moreover, the Er(8) values of all the materials in the rubbery plateau region at temperatures above Tg, and the values of the U and L types, were larger than that of ACR. The materials examined had a high molecular weight, which would restrict molecular flow due to entanglement or cross-linked structures. These results suggest that materials containing woven glass fibers are thermally stable, even at low temperatures, such as in the glassy state, because they have a higher Er(8) within the temperature range of the transition or rubbery plateau regions, compared with that of ACR.

Two types of woven glass fibers (Codes, P and S) were added to the materials in this study. The Er(8)-temperature curves of the specimens containing each type behaved similarly (Figs. 4 and 5). However, the Er(8) values of the specimens containing S were larger than those of P for all insertion positions (Table 2), and for all temperatures from 20 to 140°C. The P and S fibers differ in thickness, density, and fiber architecture, although they have the same composition (E-glass). Consequently, these results indicate that the fiber volume fraction and fiber architecture are important factors in inhibiting the flow of PMMA denture base resin, because of the higher brittleness of the glass fiber itself.

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