Dynamic viscoelastic properties and the age changes of long-term soft denture liners

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The dynamic viscoelastic properties of long-term soft denture liners were measured over a wide range of frequencies using a dynamic viscoelastometer based on a non-resonance forced vibration principle. Changes in properties over a 3 year period have also been monitored. One acrylic material, one fluoroelastomer, one heat cured silicone and one self curing addition silicone were used. Complex dynamic tensile modulus (E*), tensile storage modulus (E'), tensile loss modulus (E") and loss tangent (tan δ) were determined over the frequency range from 0.01 to 100 Hz on administration of a 0.27% strain at 37 °C. The dynamic viscoelasticity of the acrylic and fluoroelastomer products was more sensitive to changes in frequency than that of silicone products. The acrylic material and fluoroelastomer exhibited viscoelastic behaviour whilst silicones exhibited elastic behaviour. The silicone products remained unchanged after soaking for 3 years whilst the acrylic and fluoroelastomer products underwent significant change.

KEY WORDS: Soft denture liners, Dynamic viscoelasticity, Frequency, Age changes, Non-resonance forced vibration method

Long-term soft denture liners have been used in Prosthodontics for patients who are unable to tolerate conventional hard-based acrylic dentures because of thin and relatively non-resilient mucosa or severe alveolar resorption[1].

The efficacy of soft denture liners is considered to be influenced by their viscoelastic properties and their durability. The materials should have a sufficient cushioning effect to distribute and absorb functional stress, and should remain stable over time. The materials used are of several types[2], for example silicone, acrylic, and fluoroethylene which exhibit a wide range of viscoelastic properties and differ in the way in which their properties changes over time.

In previous studies, the flexibility, compliance and viscoelastic properties of soft liners have been characterized using a puncture strength test[3], creep test[4] and stress relaxation test[4,5]. These static measurements have provided valuable information on how material behaviour changes over time. However, these methods are not suitable for rigorous evaluation of the rheological characteristics of materials. Such a method should be able to adequately compare meaningful rheological parameters using a cyclic application of stress which reflects masticatory function. One instrument which is suitable for meeting this requirement is an automatic dynamic viscoelastometer based on a principle of non-resonance forced vibration. This dynamic mechanical test has been used previously to evaluate the viscoelastic properties of various materials[6,7]. In the clinical situation, denture liners are exposed both to a rapidly applied forces caused by mastication or swallowing and to a more long-term force caused by functional pressure or changes in the oral supporting tissues. In order to develop a clinically meaningful test for denture soft liners it is necessary to consider the wide range and nature of the applied forces as well as changes which occur over time and it is surprising that such an approach has not been reported before.

The purpose of this study was to evaluate dynamic viscoelastic properties of various types of long-term soft denture liners over a wide range of frequency and to monitor how the behaviour changes with age, using a dynamic viscoelastometer based on the principle of non-resonance forced vibration.

MATERIALS AND METHOD

Materials

Table 1 gives details of the four long-term soft denture liners used in the study. One acrylic material, one fluoroelastomer, one heat cured silicone and one self curing addition silicone were used. Five specimens of each material were prepared to 2 mm thickness (30mm long X 10mm wide) according to the manufacturer's instructions. The specimens were stored in distilled water at 37 °C except during the measuring period.

Measurement

Dynamic viscoelastic properties of the test materials were determined using an automatic dynamic viscoelastometer (Rheovibron DDV-25FP, Orientec Corp., Tokyo, Japan) (*Fig. 1*). This device is based on the principle of non-resonance forced vibration and consists of a measurement operation block, high/low constant temperature chamber, main unit, power unit, data processing device and testing jigs. The main unit performs high speed analogue-to-digital, digital-to-analogue conversion and transmits input-output signals to the measurement operating block, high/low temperature chamber and data processor. The measurement operating block consists of a magnetic exciter, tension control motor, amplitude detecting sensor and amplifier, load detecting load cell and chucks. During testing a suitable tension is applied to the loaded specimen and the dynamic displacement, i.e. sine wave vibration (sinusoidal stress), is added as a forced power. At the other end of the specimen, the dynamic load is detected and this is converted to familiar rheological parameters such as dynamic strain and dynamic stress, complex dynamic tensile modulus (E*), tensile storage modulus (E'), tensile loss modulus (E") and loss tangent (tan δ).

A series of dynamic mechanical tests was conducted at 37 °C, and at the following times after specimen preparation: 24 hours, 30days, 60days, 120days, 6months, 12months, 2 years and 3 years. E*, E', E" and tan δ were determined over a frequency range of 0.01 to 100 Hz (at 37 frequency measuring points) on administration of a 0.27% strain. The distance between the two chucks was 15 mm.

Three-way ANOVA testing was performed to determine whether statistically significant differences existed between materials, times and frequencies for E', E" and tan δ. Three frequencies of 0.05, 1 and 100 Hz were selected from the 37 frequency measuring points for statistical analyses. The differences of these values among the materials and those among the time of storage of each material were tested with the Student-Newman-Keuls test at the 5% level of significance.

Analysis of dynamic viscoelasticity

Figure 2 shows a schematic representation of the relationship between stress and strain, with a sinusoidally varying stress, for a perfectly elastic material, a viscoelastic material and perfectly viscous liquid respectively. For a perfectly elastic solid, the strain is exactly in phase with the stress. For a perfectly viscous liquid, the strain is 90° out of phase. In the case of a viscoelastic material, the strain is somewhere in between ($\pi/2 > \delta > 0$)^8. The complex modulus E*, which is determined experimental by applying a sinusoidal stress, is resolved into two components, i.e. storage modulus E' and loss modulus E", shown vectorially in *Figure 2* . E' is the ratio of the stress in phase with the strain to the strain, whereas E" is the ratio of the stress 90° out of phase with the strain to the strain. E' represents the elastic component of material behaviour and it directly proportional to the energy storage in a cycle of deformation. E" represents the viscous component of material behaviour and it directly proportional to the average dissipation or loss of energy as heat in a cycle of deformation. The tangent of the phase angle (δ) between stress and strain, the loss tangent (tan δ), is a useful parameter and a measure of the ratio of energy lost to energy stored during cyclic deformation.

The complex modulus E^* of each material is calculated as follows:

$$|E^*| = \Delta F/S \times Lt/\Delta L$$

where ΔF = the dynamic load; S = area of specimen; Lt = length of specimen and ΔL = dynamic displacement.

The storage modulus E' and loss modulus E", are defined as:

$$E^* = E' + iE''$$

$$E' = |E^*| \cos\delta$$

$$E'' = |E^*| \sin\delta$$

where $i = \sqrt{-1}$.

The loss tangent tan δ is given by:

$$\tan\delta = E''/E'$$

RESULTS

There were significant differences between materials and significant effects of both time and frequency for E', E" and tan δ (Tables 2 to 4) as shown by 3-way Analysis of Variance. Significant interactions between material, time and frequency show that the dynamic viscoelastic properties of some materials were more affected by time of storage and frequency than others.

Figures 3 and 4 show the dependence of E*, E' and E" and tan δ on frequency for the four materials 24h after specimen preparation. The acrylic material CSS and fluoroelastomer KD exhibited higher values of E*, E' and E" at higher frequencies, whereas the silicones MB and TSR showed relatively little change with frequency. Tan δ of CSS increased as the frequency increased from 0.01 to 10 Hz, then decreased again at higher frequencies. Tan δ for KD increased with increasing frequency. MB and TSR exhibited almost no change of tan δ with frequency.

Figure 5 shows the relationship between E' and E" for the four soft denture liners at 1 Hz, 24h after specimen preparation. The values at 1Hz are important because they simulate the masticatory rhythm. There were marked differences in E', E" and tan δ at 24h among the four materials. KD had highest E' (3.50 MPa). No significant differences were found between CSS and TSR, which had significantly lower E' (1.85 and 1.98 MPa, respectively) ($p < 0.05$) than the other two materials. On the other hand, CSS had the highest E" (2.02 MPa), and MB and TSR had the lowest E" (0.09 and 0.10 MPa, respectively). No significant differences were found between MB and TSR. The order of tan δ values at 1 Hz and 24h were CSS (1.089) > KD (0.363) > TSR (0.048) > MB (0.028). All differences were significant ($p<0.05$).

E' and E" of the four materials at 0.05 and 100 Hz 24h after specimen preparation, are shown in *Figures 6 and 7*, respectively. There were marked differences in both E' and E" for each material at 24h when tested at 0.05 Hz and 100 Hz. Values of E' were significantly higher than E" for all materials at 0.05 Hz ($p<0.05$). MB had the highest E' (2.93 MPa) and CSS had the lowest E' (0.86 MPa) at 0.05 Hz, i.e. under virtually continuous pressure. Values of E" of MB and TSR were significantly lower than those of the other two materials ($p<0.05$). At 100 Hz, CSS had the highest E' (34.50 MPa) and E" (43.32 MPa), and MB and TSR had the lowest E' (3.23 and 2.19 MPa, respectively) and E" (0.14 and 0.15 MPa, respectively). This represents material behaviour against an instantaneously applied pressure. Only for CSS was E" significantly higher than E' at 100 Hz ($p<0.05$). CSS and KD exhibited higher tan δ than MB and TSR over the entire experimental frequency range.

Variation of E', E" and tan δ with time of storage for the four materials at 1 Hz is depicted in *Figures 8 through 10.* E', E" and tan δ of the acrylic material CSS increased most significantly with storage time over 3 years. E' of CSS became significantly higher ($p<0.05$) than that of MB and TSR at 3 years. The fluoroelastomer KD exhibited significant change of E', E" and tan δ with time ($p<0.05$). Changes in properties on storage for 3 years were small and mainly insignificant for the silicones MB and TSR.

DISCUSSION

Some edentulous patients have an irregular mandibular alveolar bone, covered by a thin and relatively non-resilient mucosal tissue. When masticatory or functional forces are transferred to the denture foundation area through a hard denture base, this supporting tissue can be damaged, resulting in chronic soreness, abused tissues and bone loss[9]. Long-term soft denture liners are used for such patients to cushion the transmitted forces and relieve pain[1,9,10]. The viscoelastic properties and durability of the materials used as denture linings are thought to be among the major factors which affect clinical success[6,11].

Soft denture liners are subjected both to instantaneous pressure during mastication and to the continuous pressure, of a lower magnitude, of the oral mucosa during resting. Furthermore, in general, polymers behave in a more elastic fashion in response to a rapidly applied force and in a more viscous in response to a slowly applied force. Therefore, three specific frequency points (0.05, 1 and 100 Hz) were selected for statistical analyses. The value of 1 Hz reflects typical masticatory conditions. Those of 0.05 Hz and 100 Hz indicate behaviour under functional forces and very rapidly applied forces respectively. These values, especially 1 Hz and 0.05 Hz, are considered to be important in assessing the clinical significance of the results because they reflect the clinical environment.

The dynamic viscoelastic properties of polymeric solids are measured mainly by one of three methods; namely, the free tortional vibration method, resonance forced vibration method and non-resonance forced vibration method. The free torsional vibration method, in which the free damped oscillation of a torsion pendulum is used, has been used to measure the viscoelastic properties of soft lining materials[6]. However, this method is limited at the low end of the frequency range (less than 0.1 Hz) due to the effect of air resistance. The resonance forced vibration method also operates most effectively at high frequencies (greater than 10 Hz) and requires large specimens for accurate measurements[7]. The dynamic viscoelastometer based on the principle of a non-resonance forced vibration was used in this study in order to overcome the deficiencies of the other two methods. The method enables the frequency-dependent properties of soft denture liners to be determined over a wide range of frequencies (0.01 - 100 Hz) and thus allows predictions of behaviour under conditions which are relevant to the clinical situation to be evaluated.

Three-way ANOVA testing was performed in this study. Since there are significant interactions between the variables any comparison of materials could produce a different result depending upon the age of the specimens and the frequency at which they are tested. Hence it is most important to select a clinically appropriate value of frequency for material comparisons. Likewise it is important to select clinically relevant times (long and short term) at which to make comparisons. Both of these factors have been properly considered and controlled in the current study.

Large differences in dynamic viscoelastic properties were found among the materials. The dynamic viscoelastic behaviour of the acrylic material and fluoroelastomer showed sensitivity to changes in frequency, whilst that of the silicones was not markedly frequency dependant. The acrylic and fluoroelastomer materials had higher loss moduli, E", and loss tangent, tan δ, than the silicones over the whole frequency range tested. The fluoroelastomer, which had the highest storage modulus, E', at 1 Hz, exhibited greater elasticity under the influence of a rapidly applied pressure representing mastication. The storage modulus E' describes elastic deformations under stress whilst the loss modulus E" describes viscous deformations. The silicones had almost no viscous component, whilst the acrylic material and fluoroelastomer had both elastic and viscous components. That is, the acrylic material and fluoroelastomer demonstrated viscoelastic properties, and the silicones were found to be elastic. For materials which have a higher value of loss tangent, energy used to deform the material is dissipated as heat and to cause changes in the polymeric structure by movements of polymeric segments or atomic grouping. These movements may not be completely reversible and may therefore result in permanent deformation of the material. At temperatures above the glass transition temperature, the attenuation of a polymeric material is reduced by crosslinking[12]. A perfectly elastic solid does not exhibit attenuation. Clinically, the damping which results from a higher value of loss tangent is likely to produce a degree of stress relief under masticatory or functional forces. Therefore, the acrylic and fluoroelastomer materials may have a greater ability to distribute stress and a better capacity for preventing transmission of the applied forces to the oral mucosa, resulting in relief of pain.

Durability of long-term soft denture liners is relevant to their continued efficacy over the lifetime of the denture and in this work changes in the dynamic viscoelasticity over time in water storage_varied markedly amongst the four materials. The acrylic material showed a greater increase in the storage modulus E', loss tangent tan δ and especially loss modulus E" with the passage of time than the other materials. Acrylic denture liners undergo two processes when immersed in water[13]. The low molecular weight plasticizer is leached out into the water and, at the same time, water is absorbed into the polymer structure. The loss of plasticizer appears to be the most important process as far as properties are concerned since ageing results not only in a dimensional change but also a loss of softness and resilience which is expressed in the current work by an increase in the storage modulus E'. The increase in loss tangent, tan δ, with time may be due to absorption of water, which potentially behaves as a plasticizer[12]. However, it can readily be appreciated that the processes of water absorption and leaching are related whilst also being likely to have a diametrically opposite affect on properties, confirming that the overall relationship between properties and age is a complicated one. Furthermore, there are many factors involved in the ageing of the soft denture liners such as effects of saliva, denture cleansers, masticatory force and thermocycling. Age changes in the viscoelasticity at the clinical situation may be larger than those observed in this study. The self curing addition silicone remained the most stable over time and the change over time for the heat cured silicone was also small. This was probably due to the low water absorption and solubility of these materials[13]. The setting reaction of the self curing addition silicone product used in this study does not involve the production of by-products after cross-linking and this almost certainly contributes to the stable nature of this material[14]. Most self curing silicone soft denture liners are cross-linked by condensation and ethyl alcohol is produced as a by-product. It has been reported that there is little difference in the percentage absorption and solubility between artificial saliva and distilled water for the soft denture liners that do not contain a plasticizer or by-product[13]. Therefore, silicones used in this study probably remain stable even in artificial saliva. The fluoroelastomer exhibited an intermediate change over time compared with the other materials.

An ideal long-term soft denture liner would, on the one hand, behave as an elastic material under the forces of mastication, in order to maintain the dimensional integrity of the lining. On the other hand it would also have viscous behaviour in order to distribute and absorb masticatory or functional forces transmitted by prostheses to the underlying tissues. A material which most closely approaches the ideal would therefore have a higher storage modulus E' and loss tangent tan δ. Considering primarily viscoelastic properties, the acrylic material and fluoroelastomer, which show viscoelastic behaviour and a greater of cushioning effect, may best meet the requirements for a soft denture liner. However, from the standpoint of durability, the silicone products may be better. The fluoroelastomer material offers a compromise based upon its viscoelastic behaviour, combined with good elasticity against instantaneously applied forces, and relatively stable durability.

CONCLUSIONS

Dynamic viscoelastic properties of long-term soft denture liners and the changes of these properties over time were evaluated. The results of this study are summarized as follows.

1. A dynamic mechanical test using non-resonance forced vibration was suited to the determination of dynamic viscoelastic properties of long-term soft denture liners over a wide range of frequencies.
2. The dynamic viscoelastic properties of acrylic and fluoroelastomer material were sensitive to changes in frequency, whilst those of silicones were relatively constant over a wide range of frequencies.
3. Acrylic and fluoroelastomer materials exhibited viscoelastic behaviour, whilst the silicones exhibited elastic behaviour.
4. The acrylic material demonstrated a more marked change in properties over time than the other materials. The dynamic viscoelastic properties of silicones remained more stable over time whilst the change over time for the fluoroelastomer was ranked between those of acrylic and silicone products.

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Figure 1 Block diagram of the dynamic viscoelastometer.

Figure 2 Schematic representation of relationship between stress and strain of perfectly elastic solid (Hookean body) (A), viscoelastic material (B) and perfectly viscous liquid (Newtonian fluid) (C) with sinusoidally varying stress.

Figure 3 Variation of complex modulus E*, storage modulus E' and loss modulus E" with frequency for four long-term soft denture liners 24h after specimen preparation.

Figure 4 Variation of loss tangent tan δ with frequency for four long-term soft denture liners 24h after specimen preparation.

Figure 5 Relationship between storage modulus E' and loss modulus E" of four long-term soft denture liners at 1 Hz, 24h after specimen preparation.

Figure 6 Mean values of storage modulus E' and loss modulus E" of four long-term soft denture liners at 0.05 Hz, 24h after specimen preparation.

Figure 7 Mean values of storage modulus E' and loss modulus E" of four long-term soft denture liners at 100 Hz, 24h after specimen preparation.

Figure 8 Variation of storage modulus E' with time of storage of four long-term soft denture liners at 1 Hz.

Figure 9 Variation of loss modulus E" with time of storage of four long-term soft denture liners at 1 Hz.

Figure10 Variation of loss tangent tan δ with time of storage of four long-term soft denture liners at 1 Hz.

Table1

Table I Long-term soft denture liners tested.

Code	Material	Type	Manufacturer
CSS	COE Super-Soft	Acrylic Heat cured	Coe Laboratories Inc. Chicago, Illinois, USA
KD	Kurepeet Dough	Fluoroethylene Heat cured	Kurecha Co. Tokyo,Japan
MB	Molloplast-B	Silicone Heat cured	Detax Karl Huber GmbH & Co. Karlsruhe, Germany
TSR	Tokuyama Soft Relining	Silicone Cold cured	Tokuyama Corp. Tokyo, Japan

Table 2 Three-way ANOVA for the storage modulus E' of four long-term soft denture liners

Source of variation	Sum of squares	DF	Mean square	F	Significance of F
Main effects	58.127	12	4.844	5193.050	0.000
Material	19.244	3	6.415	6877.203	0.000
Time	0.518	7	0.074	79.281	0.000
Frequency	38.365	2	19.182	20565.012	0.000
2-Way interactions	39.061	41	0.953	1021.377	0.000
Material time	0.748	21	0.036	38.197	0.000
Material frequency	38.235	6	6.372	6831.796	0.000
Time frequency	0.078	14	0.006	5.967	0.000
3-Way interactions	0.178	42	0.004	4.555	0.000
Material time frequency	0.178	42	0.004	4.555	0.000
Explained	97.366	95	1.025	1098.783	0.000
Residual	0.358	384	0.001		
Total	97.725	479	0.204		

Table2

Table 3 Three-way ANOVA for the loss modulus E" of four long-term soft denture liners

Source of variation	Sum of squares	DF	Mean square	F	Significance of F
Main effects	360.481	12	30.040	9485.961	0.000
Material	269.847	3	89.949	28403.746	0.000
Time	0.694	7	0.099	31.321	0.000
Frequency	89.940	2	44.970	14200.527	0.000
2-Way interactions	47.022	41	1.147	362.155	0.000
Material time	1.074	21	0.051	16.150	0.000
Material frequency	45.916	6	7.653	2416.527	0.000
Time frequency	0.032	14	0.002	0.718	0.756
3-Way interactions	0.469	42	0.011	3.530	0.000
Material time frequency	0.469	42	0.011	3.530	0.000
Explained	407.973	95	4.294	1356.086	0.000
Residual	1.216	384	0.003		
Total	409.189	479	0.854		

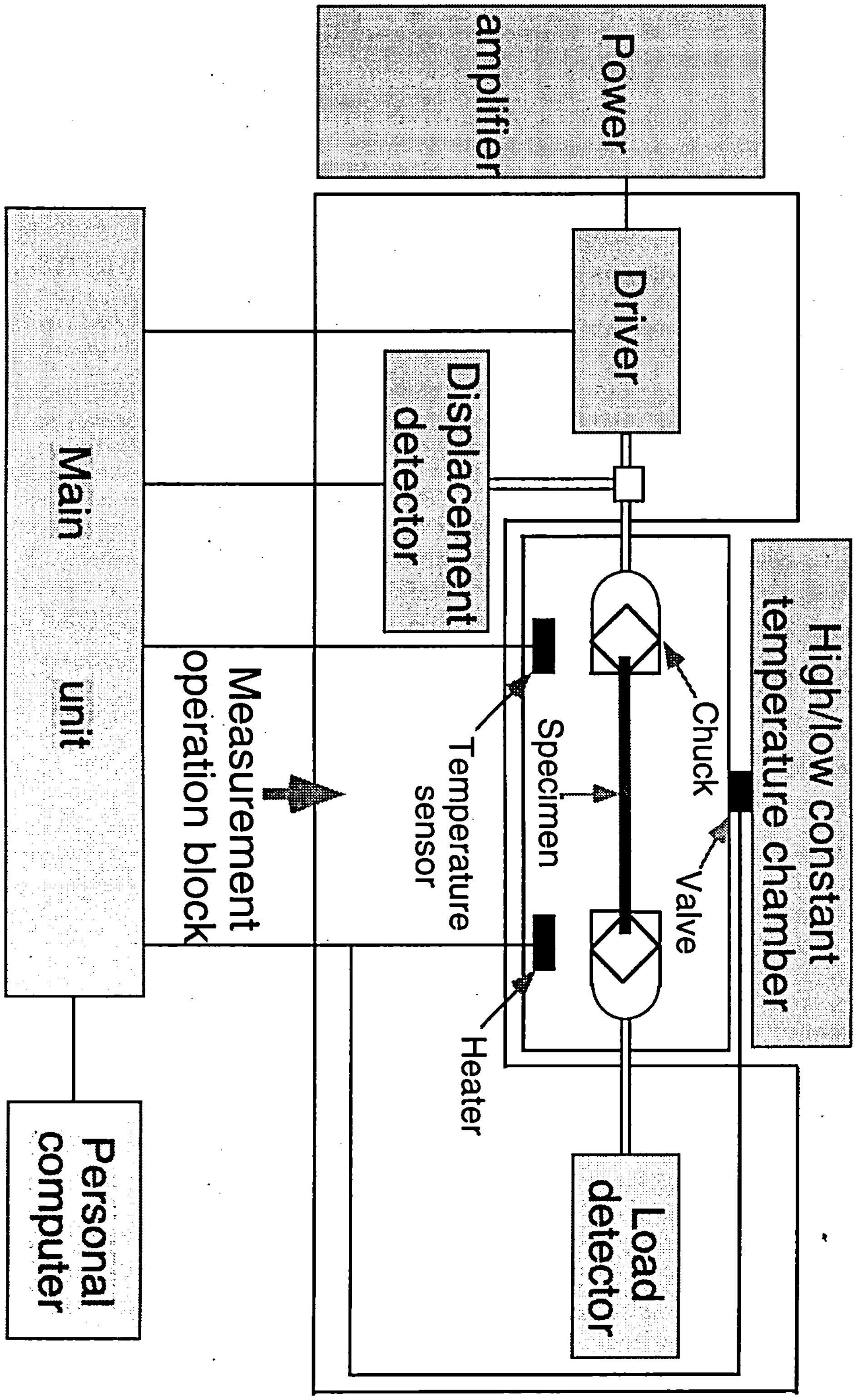
Table3

Table 4 Three-way ANOVA for the loss tangent tan δ of four long-term soft denture liners

Source of variation	Sum of squares	DF	Mean square	F	Significance of F
Main effects	158.262	12	13.189	5045.794	0.000
Material	148.434	3	49.478	18929.824	0.000
Time	1.587	7	0.227	86.734	0.000
Frequency	8.241	2	4.120	1576.461	0.000
2-Way interactions	14.933	41	0.364	139.344	0.000
Material time	4.419	21	0.210	80.506	0.000
Material frequency	7.190	6	1.198	458.456	0.000
Time frequency	3.324	14	0.237	90.834	0.000
3-Way interactions	11.589	42	0.276	105.566	0.000
Material time frequency	11.589	42	0.276	105.566	0.000
Explained	184.784	95	1.945	744.172	0.000
Residual	1.004	384	0.003		
Total	185.787	479	0.388		

Table4

Fig.1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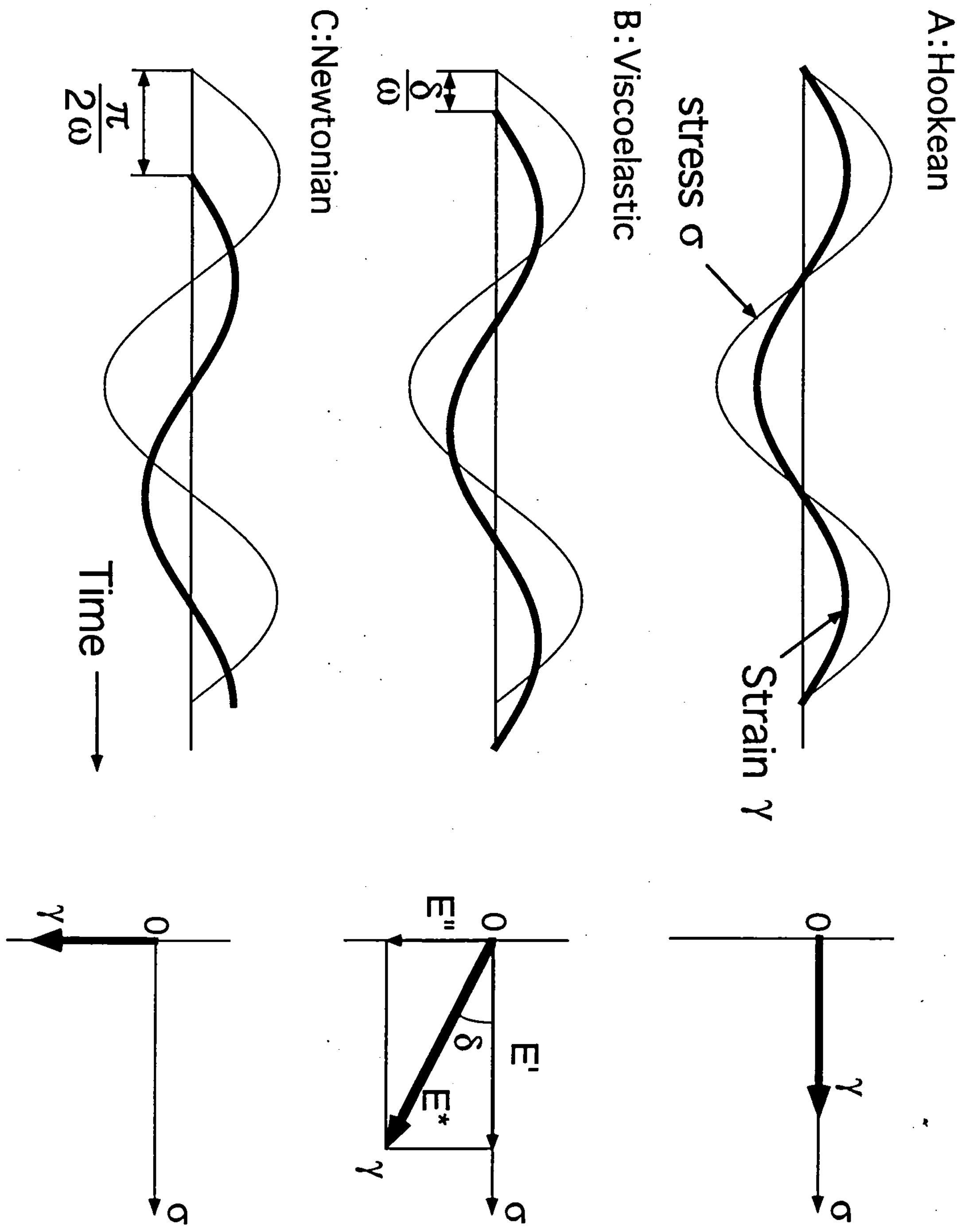
Chuck
Valve
Specimen
Temperature sensor
Heater
Load detector
Main unit
Measurement operation block
Personal computer

Fig.2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Strain γ
B:Viscoelastic
$\frac{\delta}{\omega}$
C:Newtonian
$\frac{\pi}{2\omega}$
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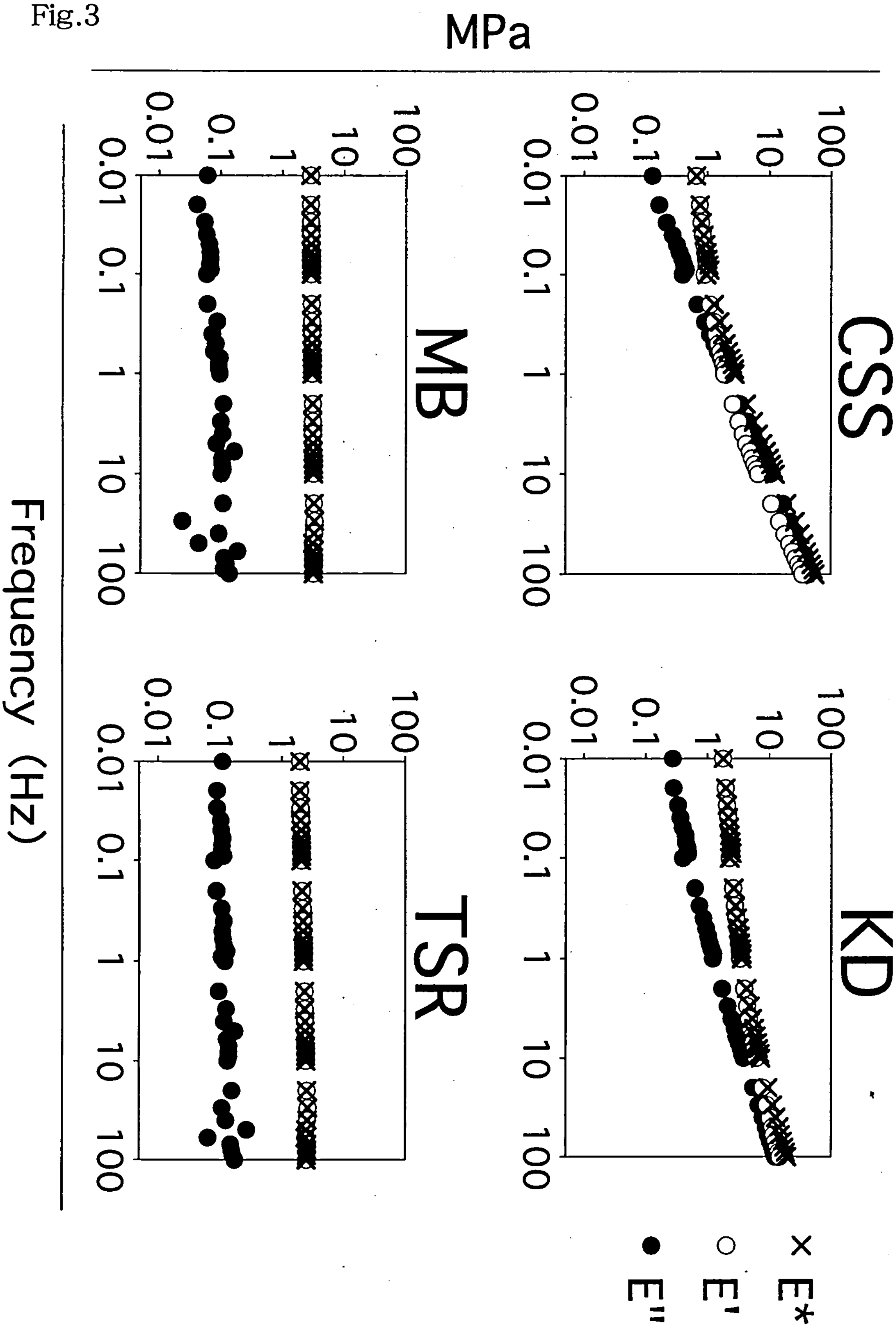
Fig.3



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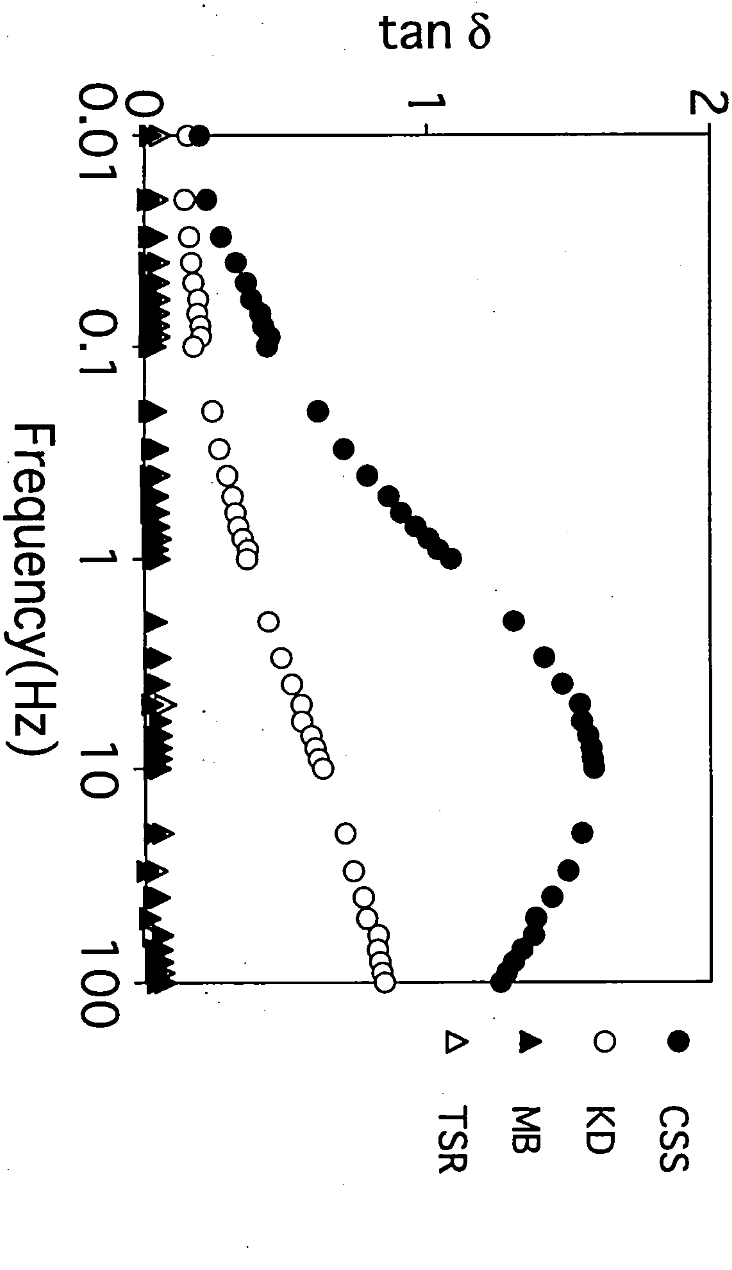
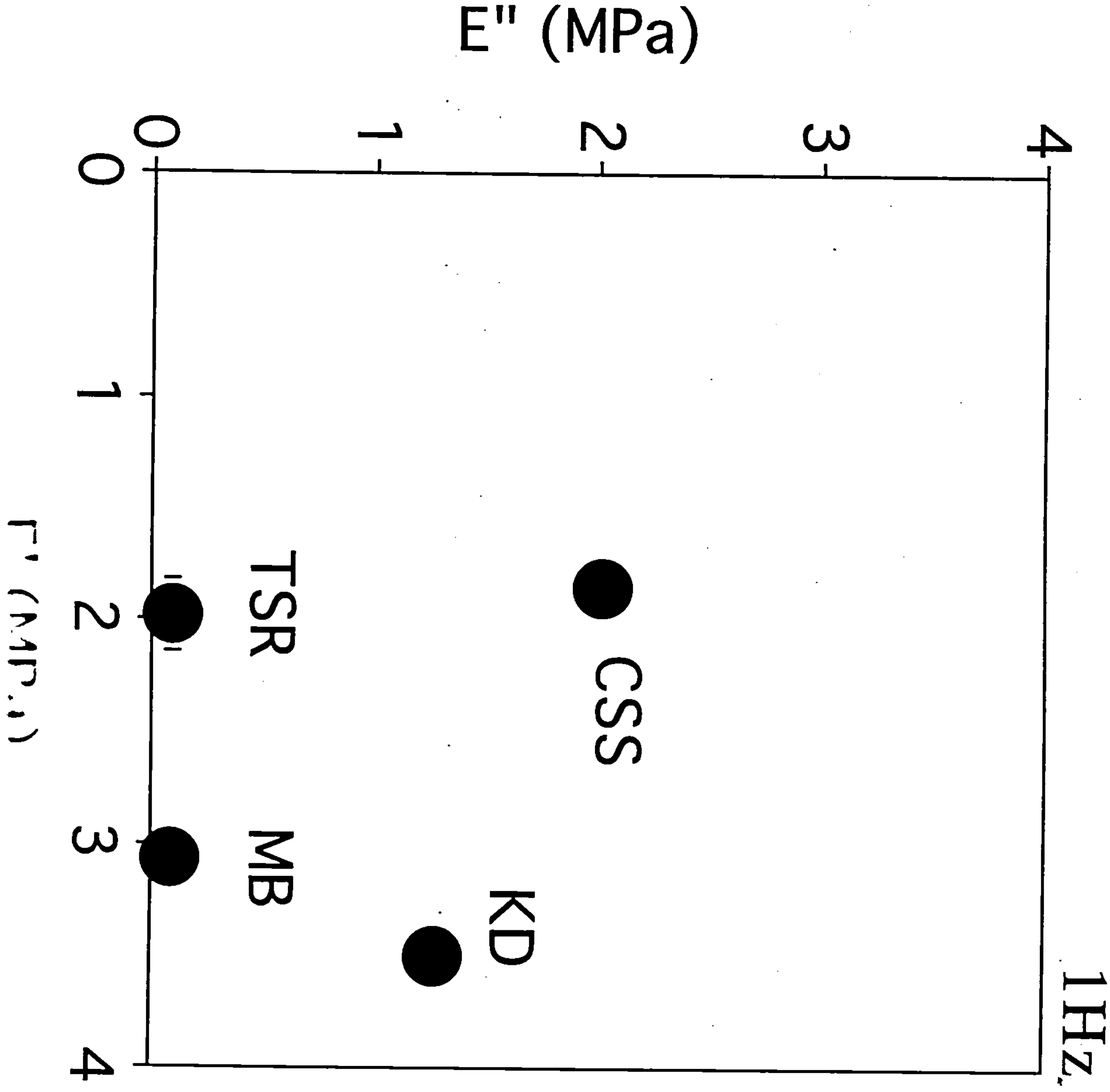


Fig.5



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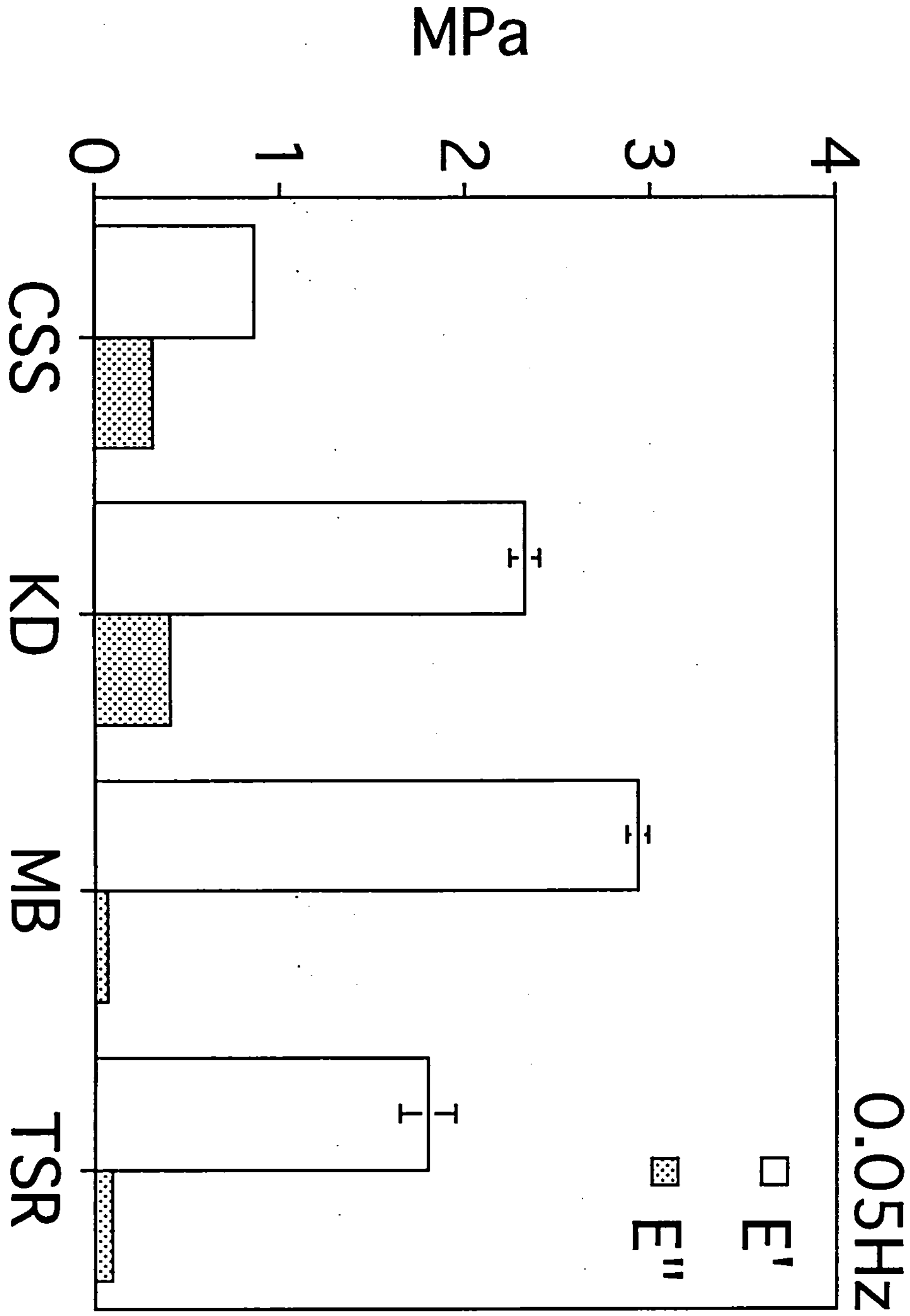

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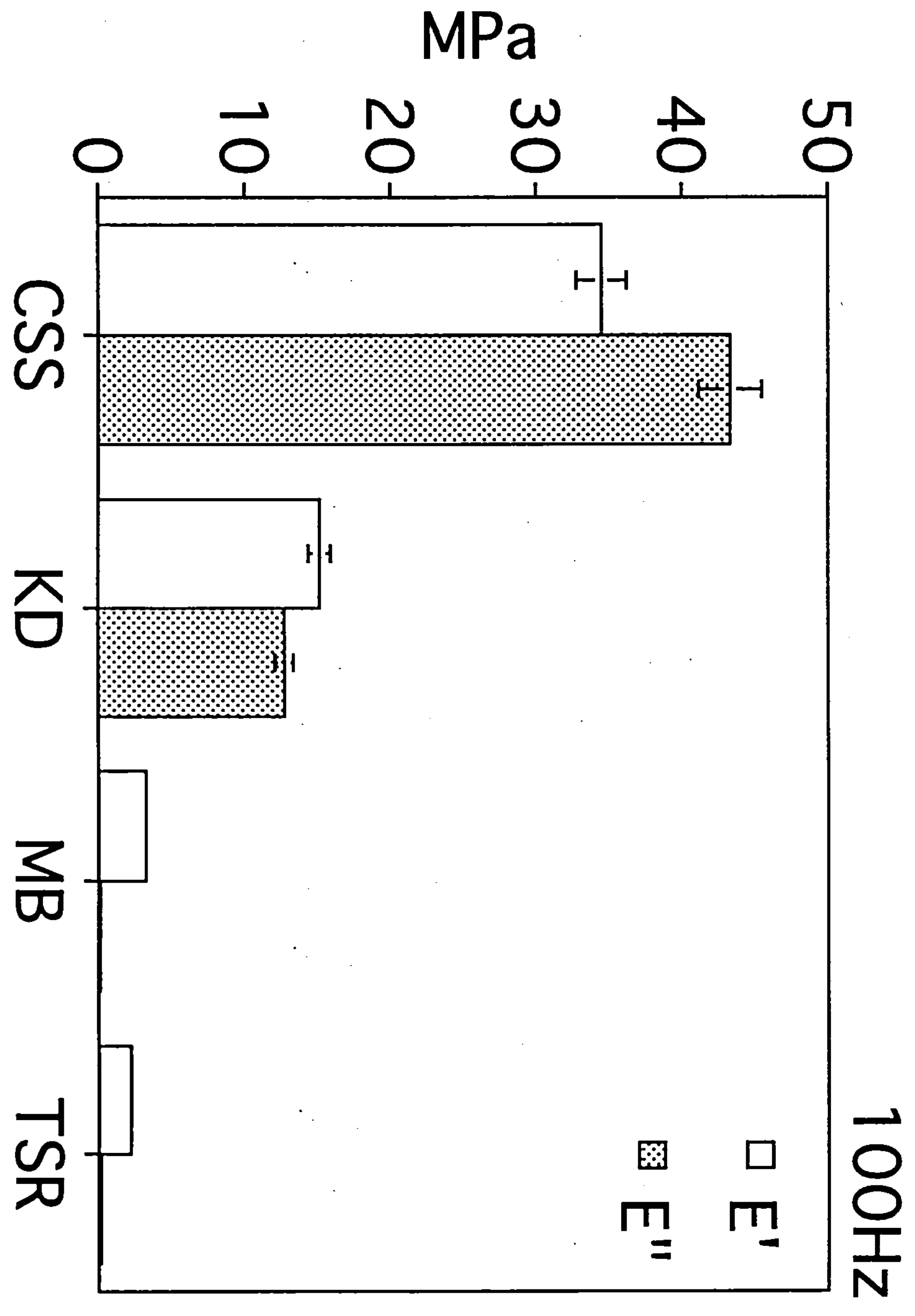

Fig.8

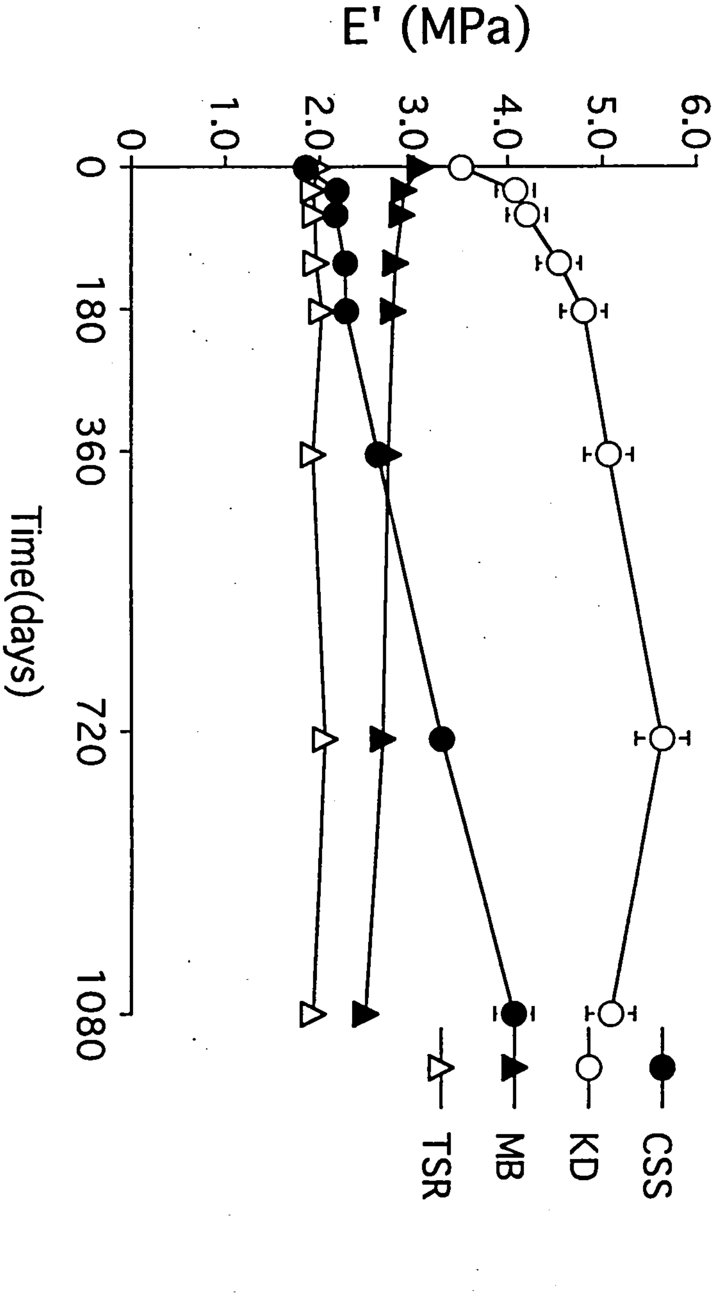

Fig.9

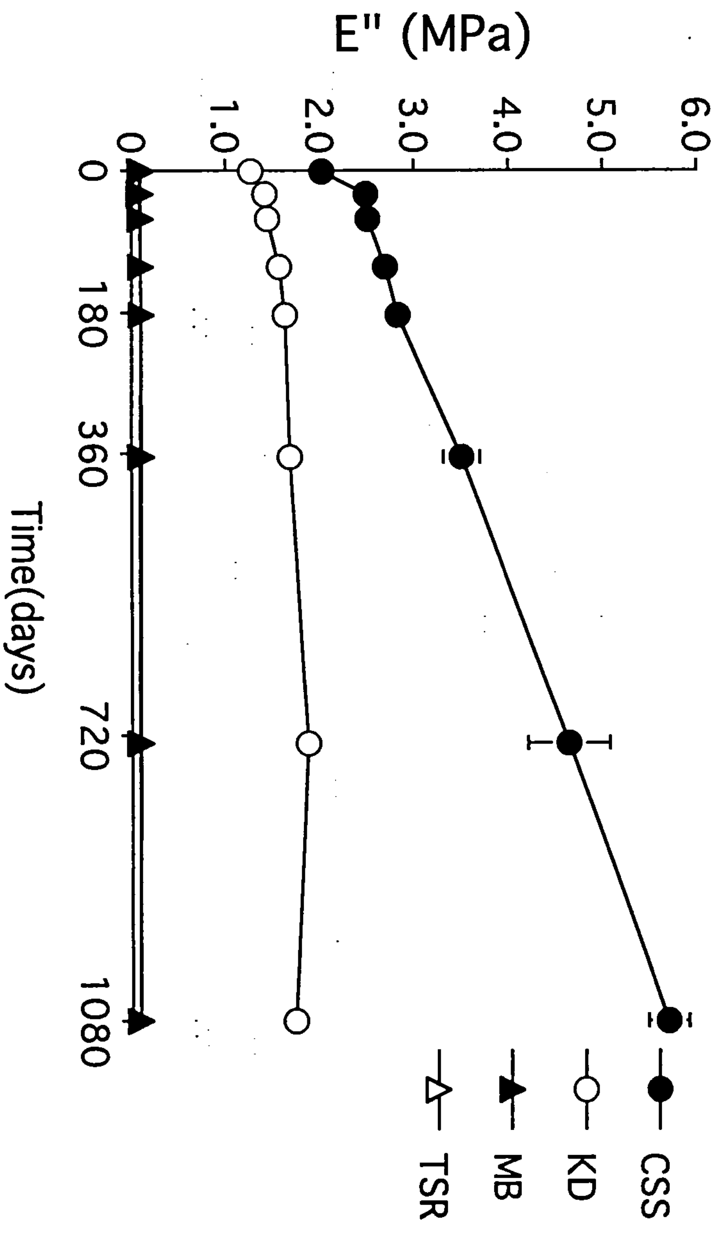

Fig.10