Effect of addition of ethyl alcohol on gelation and viscoelasticity of tissue conditioners

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Summary

The clinical effectiveness of tissue conditioners is influenced by their gelation characteristics and viscoelastic properties after gelation. The purpose of this study was to evaluate the effect of addition of ethyl alcohol on these properties, and to compare the effect of ethyl alcohol with that of the powder/liquid ratio. Three tissue conditioners were used in this study. The gelation times were obtained with an oscillating rheometer. The viscoelastic properties after gelation were also evaluated by stress relaxation tests. Addition of greater amounts of ethyl alcohol produced the shorter gelation time and the larger flow after gelation. Conversely, although the use of a higher powder/liquid ratio produced a shorter gelation time, this procedure leads to a smaller flow after gelation. The results suggested that the addition of ethyl alcohol to the liquids of tissue conditioners is an effective method for controlling gelation times and viscoelastic properties after gelation.

Introduction

Tissue conditioners are often used in the treatment of abused tissues underlying ill-fitting dentures, functional impressions, aftercare of immediate dentures, and for other clinical applications (Chase, 1961; Harrison, 1981; Qudah, Harrison & Huggett, 1990). The clinical effectiveness of these materials is influenced by their gelation and viscoelastic properties after gelation (Wilson, Tomlin & Osborne, 1966; Murata, Shigeto & Hamada, 1990; Graham, Jones & Sutow,1991). The gelation of the materials determines their working time, manipulation after mixing, and adaptation between the supporting mucosa and the denture fitting surface. The viscoelastic properties after gelation of the materials influence efficacy in the preceding applications, because the viscoelastic properties suitable for each clinical application are different.

The powder/liquid (P/L) ratio is frequently controlled to improve the handling properties of the materials or to adjust the working time. The thickness of the materials can be also altered by adjusting the P/L ratios (Newsome *et al.*, 1988). Furthermore, some manufacturers recommend alterations in the P/L ratios for different clinical situations. However, the flow properties after gelation decrease when the P/L ratio is increased to shorten the gelation time, resulting in the lower efficacy. To overcome these disadvantages, we have recently developed a method for controling the gelation times by addition of ethyl alcohol (EtOH) to the liquids of the materials.

The purpose of this study was to evaluate the effect of addition of EtOH on gelation times and static viscoelastic properties after gelation, and to compare the effect of EtOH with that of P/L ratio.

Materials and methods

Three tissue conditioners were selected for this investigation on the basis of differences in their gelation characteristics, viscoelasticity after gelation, and compositions of their liquids (Table 1). EtOH* was added to the liquids of the tissue conditioners at the

concentrations of 0, 2, 4, 6 and 8 (wt/wt)%. The standard P/L ratios recommended by the manufacturers were used. Furthermore, the range of three P/L ratios, i.e. manufacturer's recommendation and increases of P/L by 0.3 and 0.6 (CC and HC: 0.9, 1.2 and 1.5; VG: 1.2, 1.5 and 1.8), were used to evaluate the influence of P/L ratios. The liquids recommended by the manufacturers were used.

The method used for measuring gelation time has been previously reported (Murata *et al.*, 1993). The apparatus for measuring was an oscillating rheometer †. Gelation time was defined as the time required for a 75% reduction in the width of the rheometer trace (Fig. 1). Five tests were carried out for each material at 37 °C. Powders and liquids were kept at 22 ± 1 °C before testing.

The method, analysis and measuring equipment for the stress relaxation test used in this investigation are described in a previous report (Murata *et al.*, 1990). Five specimens of each material were made into disks 2mm in thickness and 18mm in diameter. A series of stress relaxation tests was conducted at 37 °C, 4 h after mixing. On administration of a 20% strain, changes in the load over a period of 5 min were recorded.

Stress relaxation curves of the tissue conditioners were evaluated by the analogies of a four-element model in which two Maxwell elements are connected in parallel (Fig. 2). In the four-element model, it can be considered that an instantaneous force works on the spring of each Maxwell element, represented by the instantaneous modulus E_0. The materials behave elastically. On the other hand, a more long-term force works on the element with the long relaxation time τ_2 as they exhibite viscoelastic behaviour. After a long period, the forces on two elements relax, and the materials behave viscously, represented by the steady-flow viscosity η_0.

If the elastic moduli are taken to be E1 and E2, the coefficients of viscosity to be $\eta 1$ and $\eta 2$, with relaxation time τ_1, τ_2, then the relaxation modulus E_r (t) for this model is defined as:

$$E\,r(t) = E\,r(0)\exp(-t/\tau 1) + Er(0)\exp(-t/\tau 2).$$

The instantaneous modulus E_0 (=Er (0)) and the steady-flow viscosity η_0, respectively, are represented as follows:

$$E_0 = E\,1 + E2 = Er\,(0)$$

$$\eta 0 = \eta 1 + \eta 2 = E1\tau 1 + E2\tau 2$$

To make comparisons among the materials, the instantaneous modulus E_0 and the steady-flow viscosity η_0, which were important factors in clinical assessment, were obtained.

Two-way ANOVAs were performed to find whether statistically significant differences were present between materials, and addition of EtOH and P/L ratios for gelation times, E_0 and $\eta 0$. The differences among materials were tested with the Tukey's method at a 5% level of significance.

Results

Figure 3 shows the effect of addition of EtOH on gelation times of the 3 tissue conditioners. Visco-Gel was found to have the longest gelation time among the 3 materials mixed with the P/L ratios recommended by the manufacturers using no EtOH-added liquids ($p < 0.05$). No significant differences were found between the gelation times of COE-Comfort and Hydro-Cast. The gelation times of COE-Comfort and Visco-Gel decreased exponentially with increasing addition of EtOH ($p < 0.05$). No significant differences were found between gelation times of Hydro-Cast produced from liquids of varying concentration of EtOH.

The effect of addition of EtOH on the instantaneous modulus E_0 and the steady-flow viscosity $\eta 0$ of the 3 tissue conditioners is shown in Fig. 4. Visco-Gel was found to have the highest E_0 and $\eta 0$ among the 3 materials mixed with the P/L ratios recommended by the manufacturers using no EtOH-added liquids ($p < 0.05$). There were no significant differences in E_0 and η_0 between COE-Comfort and Hydro-Cast. E_0

of Visco-Gel and η_0 of COE-Comfort and Visco-Gel were significantly lower when larger quantities of EtOH were added ($p < 0.05$). The rate of change of η_0 by varying the concentration of EtOH was higher than that of E_0. There were no significant differences in the E_0 and η_0 values among EtOH-added Hydro-Cast. Although no significant differences were found among the E_0 values of EtOH-added COE-Comfort, these values tended to be lower with greater addition of EtOH.

The gelation times, E_0 and η_0 for the 3 tissue conditioners produced from various P/L ratios are shown in Figs 5 and 6. The gelation times of all the materials decreased exponentially with increases in the P/L ratios ($p < 0.05$). E_0 and η_0 of all the materials were higher at higher P/L ratios. The rate of change of η_0 by varying the P/L ratio was higher than that of E_0.

Relationships between gelation times, and E_0 and η_0 of COE-Comfort, Hydro-Cast and Visco-Gel produced from various concentrations of EtOH and from various P/L ratios are shown in Figs 7,8 and 9, respectively. Both E_0 and η_0 of COE-Comfort and Visco-Gel were lower with shorter gelation times being produced by greater addition of EtOH. The rate of change in these three values of Visco-Gel was higher than that of COE-Comfort. The addition of EtOH had no significant influence on the gelation times, E_0 and η_0 of Hydro-Cast. Conversely, both E_0 and η_0 of all the materials were higher with the shorter gelation times produced by higher P/L ratios.

Discussion

The gelation characteristics and viscoelastic properties after gelation of commercial tissue conditioners are varied because of the differences in composition and structure, (for example, P/L ratio, molecular weight and particle size of the polymer powder, EtOH content, and type of plasticizer) (Jones *et al.*, 1986, 1991; Parker & Braden, 1990; Murata *et al.*, 1993). Therefore, it is important to obtain a good understanding of the

manipulation of each material and to select a material suitable for each clinical purpose such as conditioning of abused tissues, functional impressions or temporary relining.

The initial flow and gelation of tissue conditioners have been characterized by a parallel-plate plastometer (Newsome *et al.*, 1988), a reciprocating rheometer (Jones *et al.*, 1986), an oscillating rheometer(Murata *et al.*, 1993) and a displacement rheometer (Murata *et al.*, 1997). The oscillating rheometer, which is like a reciprocating rheometer, was used in this study. This rheometer measures a complex combination of the dynamic viscosity and storage modulus of the material and a spring constant (Cook & Brockhurst, 1980) and does not measure absolute values of viscosity. However, this apparatus allows viscosities of various materials to be compared simply and conveniently.

The viscoelastic properties, compliance and flexibility of the materials have been measured with a puncture strength test (Jones *et al.*, 1986), a dynamic mechanical test (Duran, Powers & Craig, 1979), a creep test (Wilson *et al.*, 1966; Duran *et al.*, 1979) and a stress relaxation test (Murata *et al.*, 1990). The stress relaxation test, which measures the stress required to hold the deformation constant as a function of time after the specimen is quickly deformed a given amount, was used in this study. Tissue conditioners behave elastically in response to a rapidly applied force, such as bite force, and viscously in response to a continuous weak pressure of the oral mucosa, such as functional pressure during dynamic functional impression making and tissue conditioning. It is necessary to evaluate both the elasticity and viscosity of the materials. Therefore, the analogies of four-element model in which two Maxwell elements with elastic element and viscous element are connected in parallel were made in this study. For the purpose of a comparative study, the instantaneous modulus E_0 and the steady-flow viscosity η_0 were obtained for each material.

The handling and thickness of tissue conditioners are influenced by their gelation characteristics. To be effective, the layer must be of sufficient bulk and a thickness of 2 mm is recommended (Newsome *et al.*, 1988). Materials with longer gelation times are

more difficult to manipulate in terms of producing the optimum thickness because of the higher initial flow during gelation over a long time. There is also a potential for inadvertent plastic molding of these materials. The denture containing these materials must be also placed in the mouth for a longer period before removal for trimming. Therefore, dentists frequently increase the P/L ratio to produce a shorter gelation time and a thicker conditioning layer. However, this procedure results in higher stiffness and less flow after the materials gel. They also delay the placement of the denture and insert it in the mouth after the flow lessens, resulting in a longer procedure time.

Graham *et al.* (1991) reported that it would be possible to control the gelation time of a tissue conditioner by making variations in the content of EtOH, plasticizer, or the polymer combination before mixing. To overcome the preceding disadvantages, a method for controlling the gelation times of tissue conditioners by addition of ethyl alcohol (EtOH) to the liquids has been developed. Greater addition of EtOH to COE-Comfort and Visco-gel resulted in shorter gelation times and lower values of E_0 and $\eta 0$ after gelation. The liquids of the materials consist of EtOH and a plasticizer which is normally an aromatic ester such as butyl phthalyl butyl glycolate, benzyl benzoate and butyl benzyl phthalate (Braden, 1970; Jones *et al.*, 1988). The EtOH content and the type of plasticizer were found to have a significant influence on the gelation characteristics and viscoelastic properties after gelation (Jones *et al.*, 1986; Murata *et al.*, 1993). EtOH with high polar bonding facilitates penetration of the aromatic ester into the polymer particles, resulting in shorter gelation times. The higher concentrations of EtOH, which have low-viscosity, are also associated with the lower viscosity of the solution, resulting in better plasticizing effectiveness and larger flow after gelation.

There were marked differences in the effect of addition of EtOH among the materials. The gelation and viscoelasticity of Visco-Gel were affected more than those of COE-Comfort by addition of EtOH, and there was no effect on the properties of Hydro-Cast. The liquid of Visco-Gel contains a considerably lower percentage of EtOH (4.9wt%).

COE-Comfort and Hydro-Cast liquids contain 8.2 and 12.4wt% EtOH, respectively (Jones *et al.*, 1988). The materials containing the smaller percentages of EtOH in the original liquids were affected more by additional EtOH. The total percentages of EtOH in the liquid of Visco-Gel, COE-Comfort and Hydro-Cast after addition of 8wt% EtOH increased by 2.55, 1.90 and 1.56 times, respectively. The greater effect of addition of EtOH may have arisen from the higher rates of change in proportion of EtOH in the liquid. Furthermore, higher rates of change in gelation times and viscoelastic properties were found in the region of the smaller percentages of EtOH in the liquids.

The higher P/L ratios produced the shorter gelation times and then higher values of E_0 and η_0 after gelation in all the materials. Higher concentrations of powders are associated with greater polymer entanglement, resulting in shorter gelation times and smaller flow properties after gelation. There is the potential for this procedure to lower the clinical effectiveness in some clinical situation.

Tissue conditioners can be used for various clinical applications. When used to condition abused tissue underlying ill-fitting dentures, a material should flow under the continuous weak pressure caused by tissues returning to their normal position. On the other hand, for temporary relinings, a material should not flow out of the denture, to prevent the occlusal vertical dimension from changing after close adaptation to the tissues. When the dentist uses a material with a longer gelation time and smaller flow after gelation for the purpose of conditioning inflamed and distorted oral mucosa, the addition of EtOH to the liquids is recommended in order to produce a shorter gelation time and greater flow after gelation. This method is more effective in adjusting these properties of materials with smaller percentages of EtOH in the liquids. Conversely, a material with a shorter gelation time and smaller flow after gelation can be produced for the purpose of temporary relinings by increasing the P/L ratio of materials with longer gelation time and greater flow. These two techniques would be applied depending on the clinical situation.

As stated above, the results of this study suggest that the addition of EtOH to the liquids of tissue conditioners is a effective method for controlling gelation times and viscoelastic properties after gelation.

Conclusions

The effect of addition of ethyl alcohol to tissue conditioners on their gelation characteristics and viscoelastic properties after gelation was evaluated, and compared with that of the powder/liquid ratio. The results of this study are summarized as follows.

(i) A wide range of the gelation times, the instantaneous modulus E_0 and the steady-flow viscosity η_0 after gelation were found among the materials mixed with the P/L ratios recommended by the manufacturers using no ethyl alcohol-added liquids

(ii) A greater addition of ethyl alcohol produced a shorter gelation time and lower values of instantaneous modulus E_0 and steady-flow viscosity η_0. This method was more effective in the materials with smaller percentages of ethyl alcohol in the original liquids.

(iii) A higher powder/liquid ratio produced a shorter gelation time and higher values of instantaneous modulus E_0 and steady-flow viscosity η.

(iv) The addition of ethyl alcohol to the liquids of tissue conditioners is an effective method for facilitating gelation and producing the larger flow after gelation.

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Fig. 1. Rheometer trace illustrating method of determining gelation time.

Fig. 2. Schematic representation of stress relaxation curve of tissue conditioners and four-element model in which two Maxwell elements are connected in parallel.

Fig. 3. Relationships between gelation times and addition of EtOH of 3 tissue conditioners.

Fig. 4. Relationships between instantaneous modulus E_0 and steady-flow viscosity η_0 and addition of EtOH of 3 tissue conditioners.

Fig. 5. Relationships between gelation times and rate of increase in P/L ratios of 3 tissue conditioners.

Fig. 6. Relationships between instantaneous modulus E_0 and steady-flow viscosity η_0, and rate of increase in P/L ratios of 3 tissue conditioners.

Fig. 7. Relationships between gelation times, and instantaneous modulus E_0 and steady-flow viscosity η_0 of CC produced from various concentrations of EtOH and from various P/L ratios. M, liquid and P/L ratio recommended by the manufacturer; E1, 2wt% EtOH; E2, 4wt% EtOH; E3, 6wt% EtOH; E4, 8wt% EtOH; P1, +0.3 P/L ratio; P2, +0.6 P/L ratio.

Fig. 8. Relationships between gelation times, and instantaneous modulus E_0 and steady-flow viscosity η of HC produced from various concentrations of EtOH and from various P/L ratios. M, liquid and P/L ratio recommended by the manufacturer; E1, 2wt% EtOH; E2, 4wt% EtOH; E3, 6wt% EtOH; E4, 8wt% EtOH; P1, +0.3 P/L ratio; P2, +0.6 P/L ratio.

Fig. 9. Relationships between gelation times, and instantaneous modulus E_0 and steady-flow viscosity η_0 of VG produced from various concentrations of EtOH and from various P/L ratios. M, liquid and P/L ratio recommended by the manufacturer; E1, 2wt% EtOH; E2, 4wt% EtOH; E3, 6wt% EtOH; E4, 8wt% EtOH; P1, +0.3 P/L ratio; P2, +0.6 P/L ratio.

Table 1. Tissue conditioners tested

Code	Material	Manufacturer	P/L by wt.*	Batch no. powder/liquid
CC	COE-Comfort	GC America Inc. Chicago, Il. USA	0.9	090292B-021093A
HC	Hydro-Cast	Kay-See Dental Mfg. Co. Kansas City, Mo., USA	0.9	01696-19195
VG	Visco-Gel	De Trey Division Dentsply Ltd Weybridge, Surrey, UK	1.2	RF16-RG85

*P/L ratio recommended by the manufacturer

Table1

Fig.1

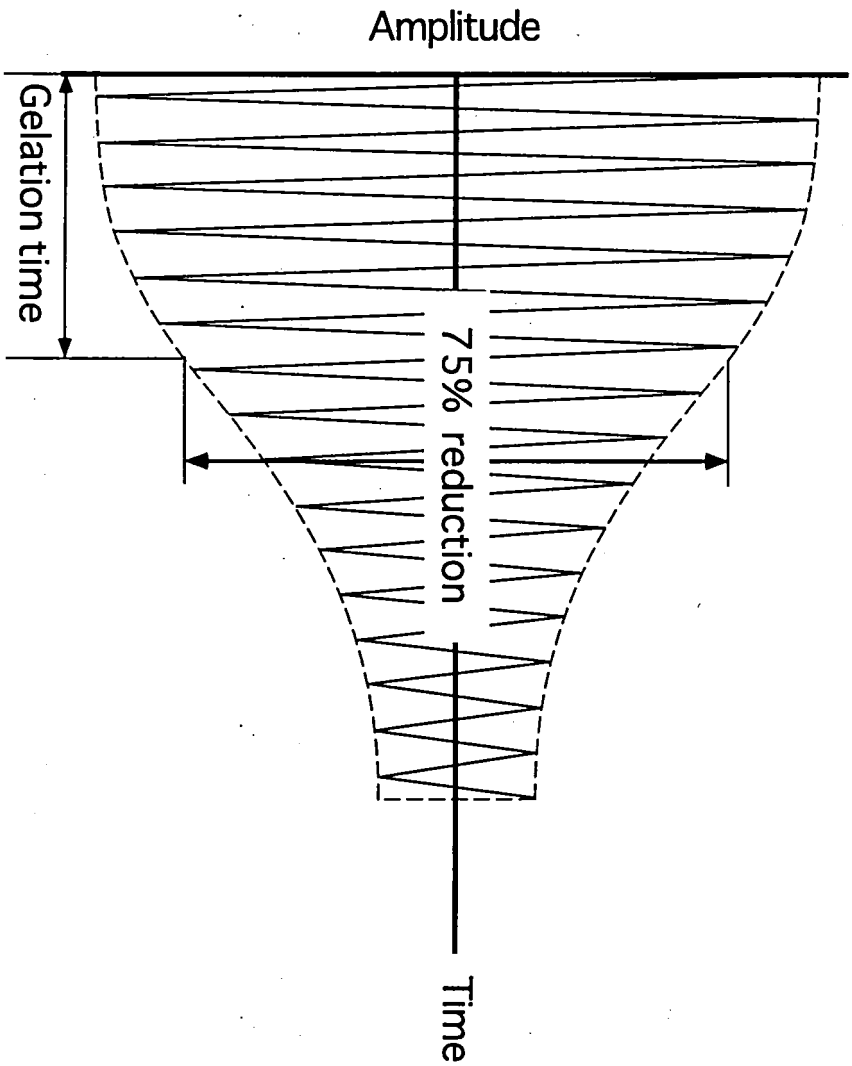


Fig.2

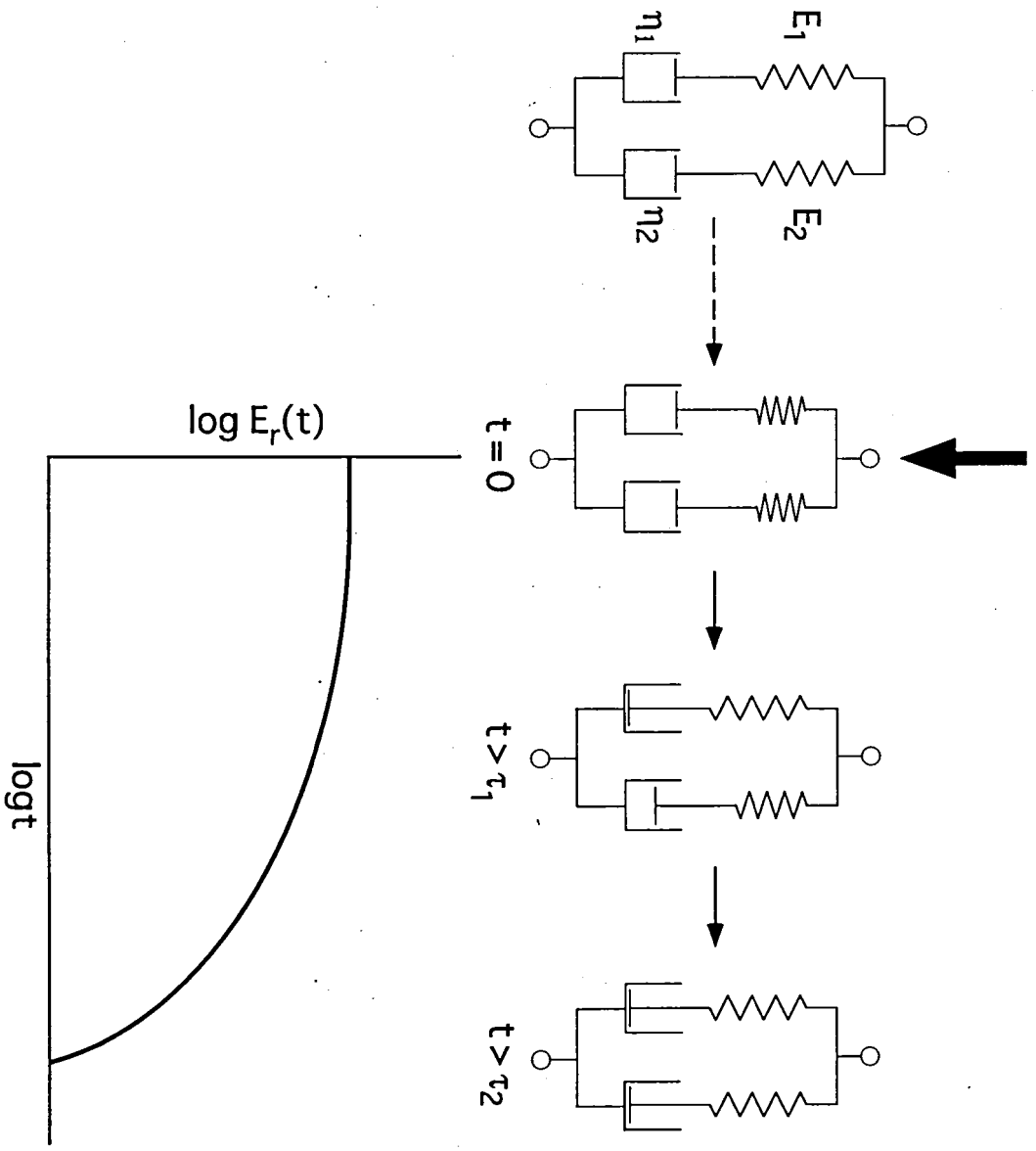


Fig.3

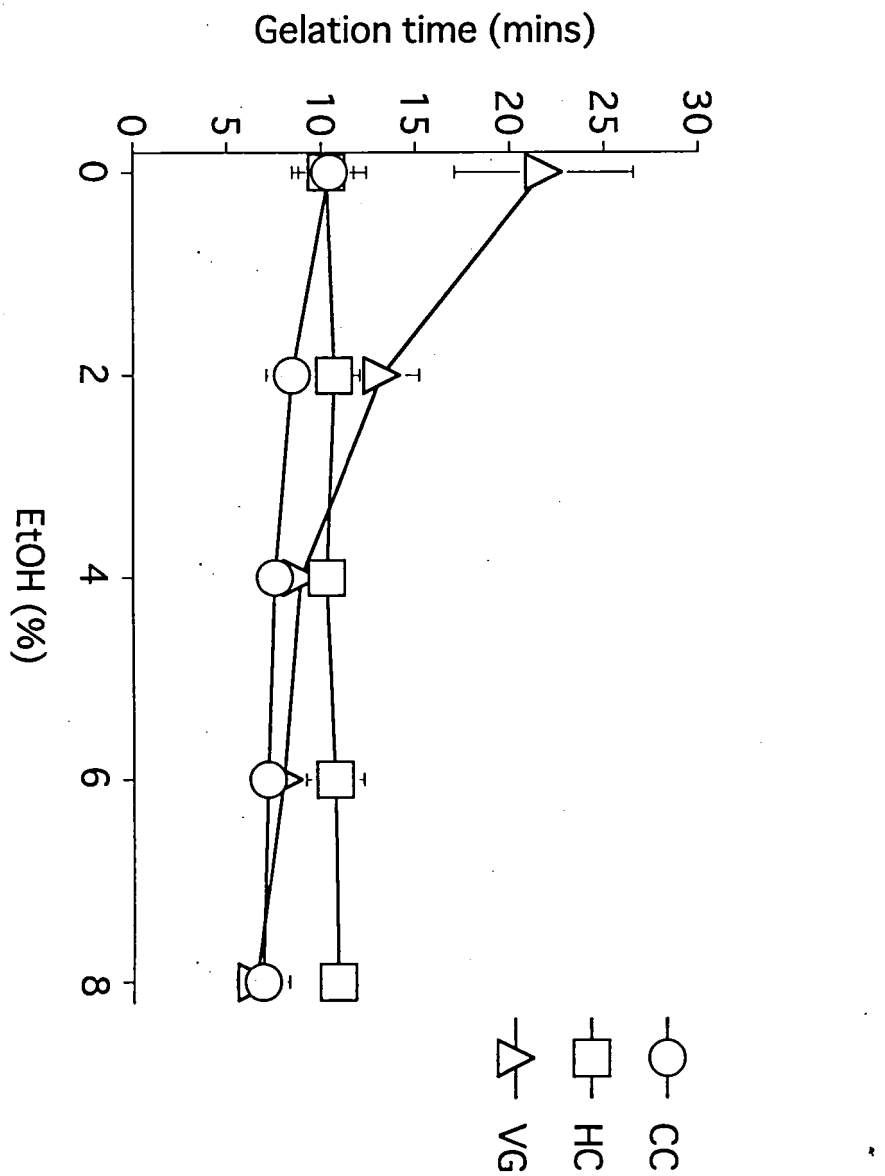


Fig.4

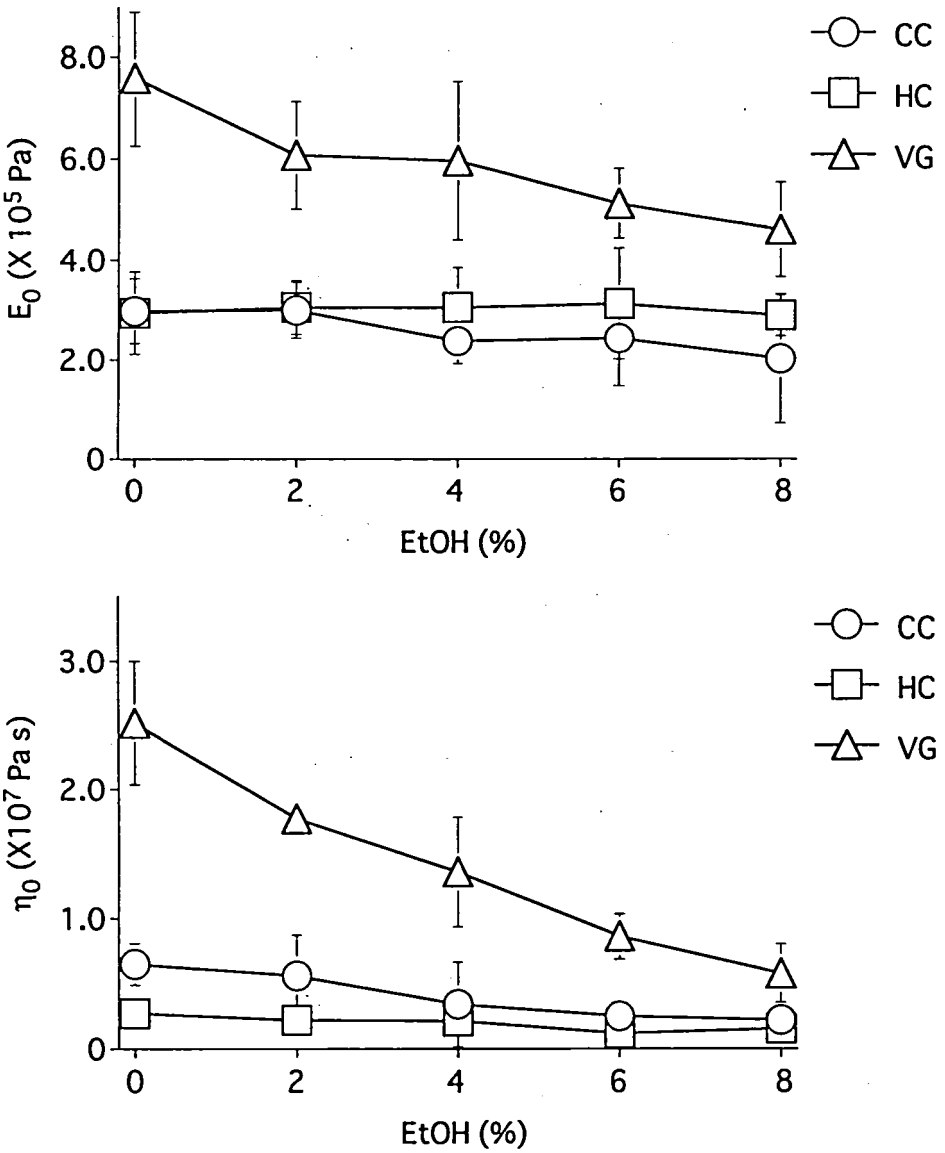

CC
HC
VG
8.0
6.0
4.0
2.0
0
E_0 (X 10^5 Pa)
0
2
4
6
8
EtOH (%)
CC
HC
VG
3.0
2.0
1.0
0
η_0 (X10^7 Pa s)
0
2
4
6
8
EtOH (%)

Fig.5

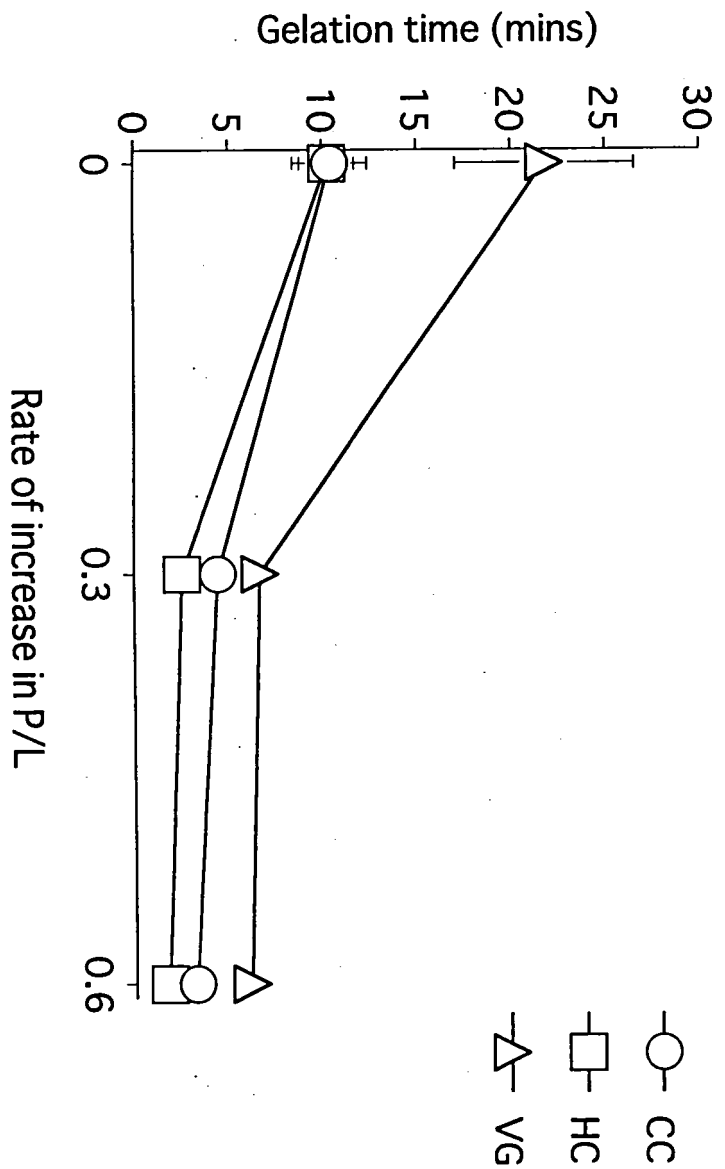

Gelation time (mins)
0
5
10
15
20
25
30
Rate of increase in P/L
0
0.3
0.6
VG
HC
CC

Fig.6

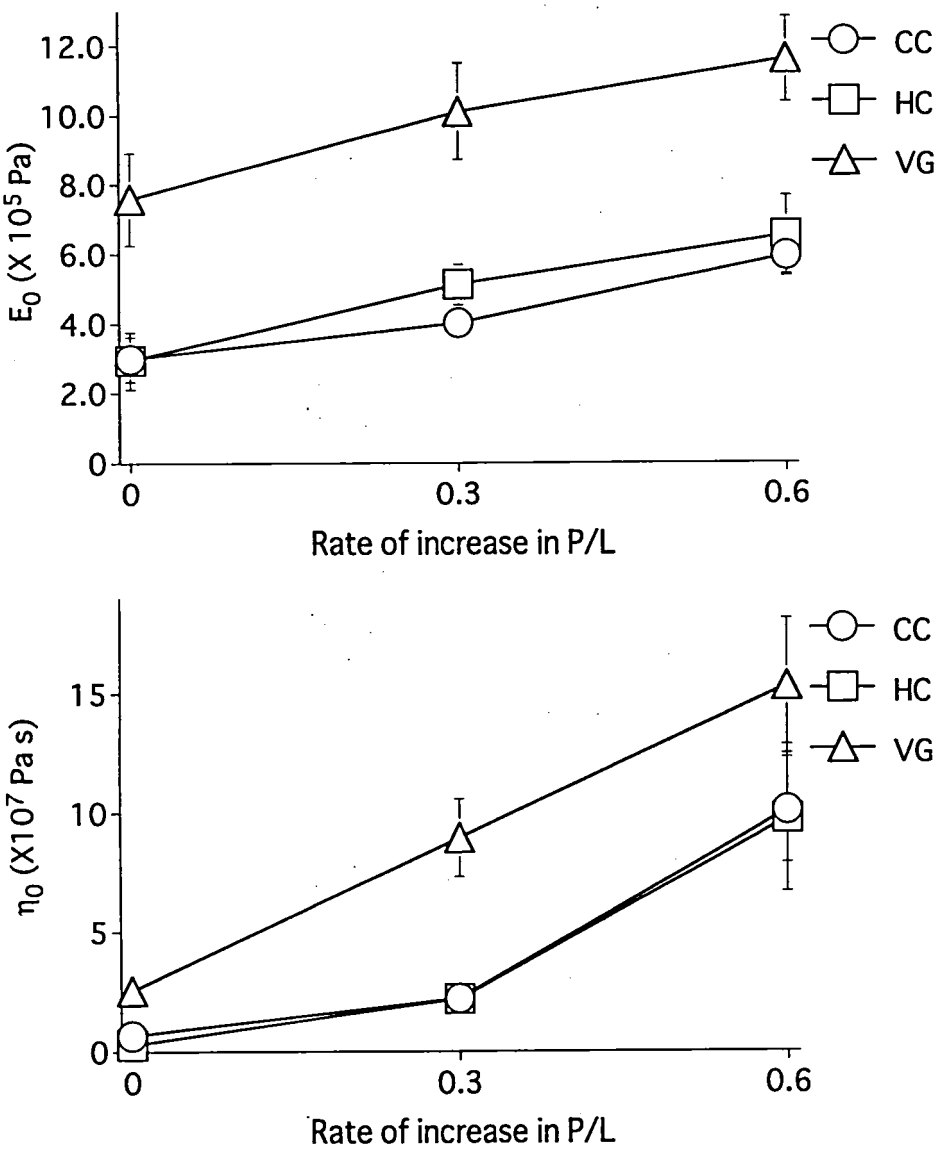

12.0
10.0
8.0
6.0
4.0
2.0
0
E_0 (X 10^5 Pa)
0
0.3
0.6
Rate of increase in P/L
CC
HC
VG
15
10
5
0
η_0 (X10^7 Pa s)
0
0.3
0.6
Rate of increase in P/L
CC
HC
VG

Fig.7

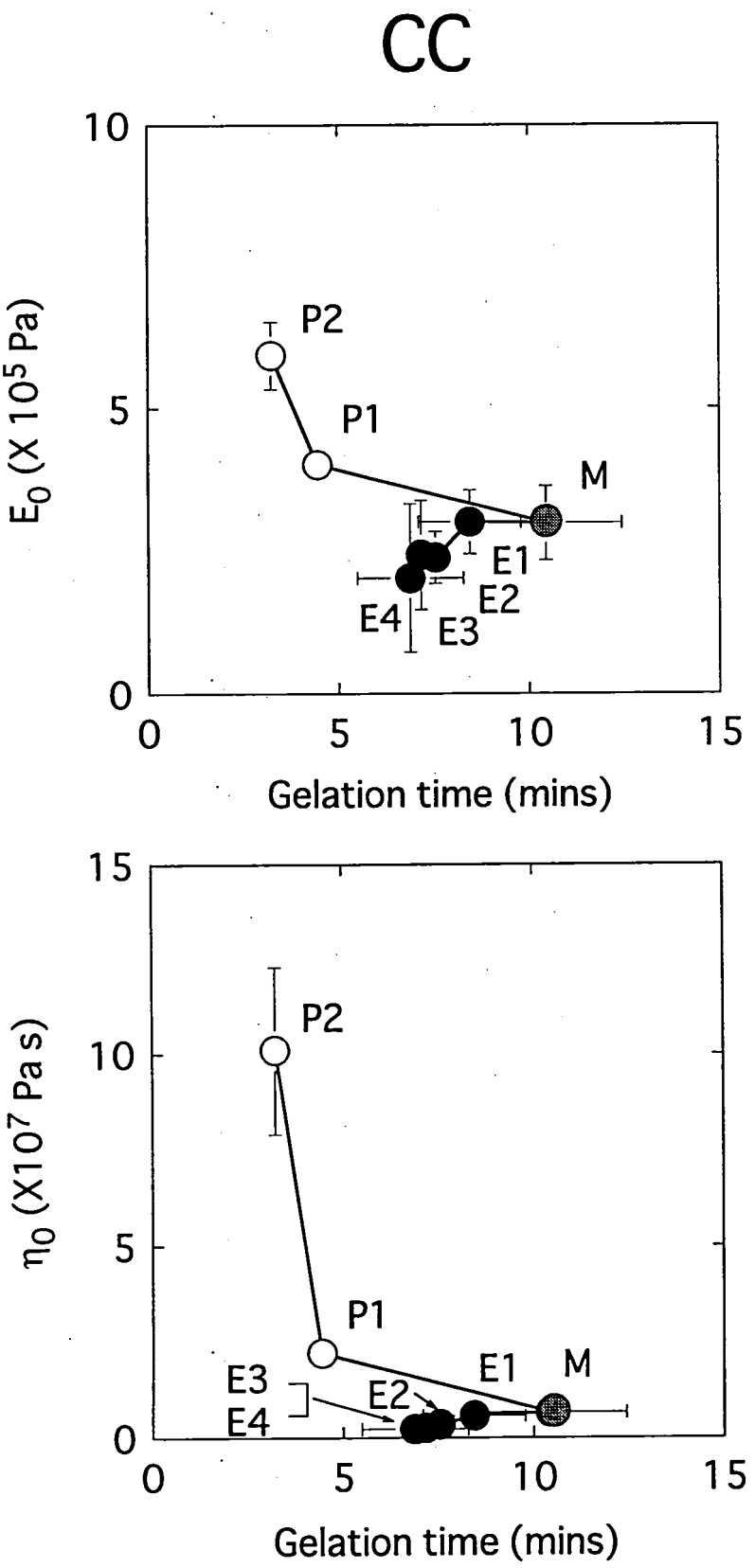

CC
10
5
0
E_0 (X 10^5 Pa)
P2
P1
M
E1
E2
E4
E3
0
5
10
15
Gelation time (mins)
15
10
5
0
η_0 (X10^7 Pa s)
P2
P1
E1
M
E3
E4
E2
0
5
10
15
Gelation time (mins)

Fig.8

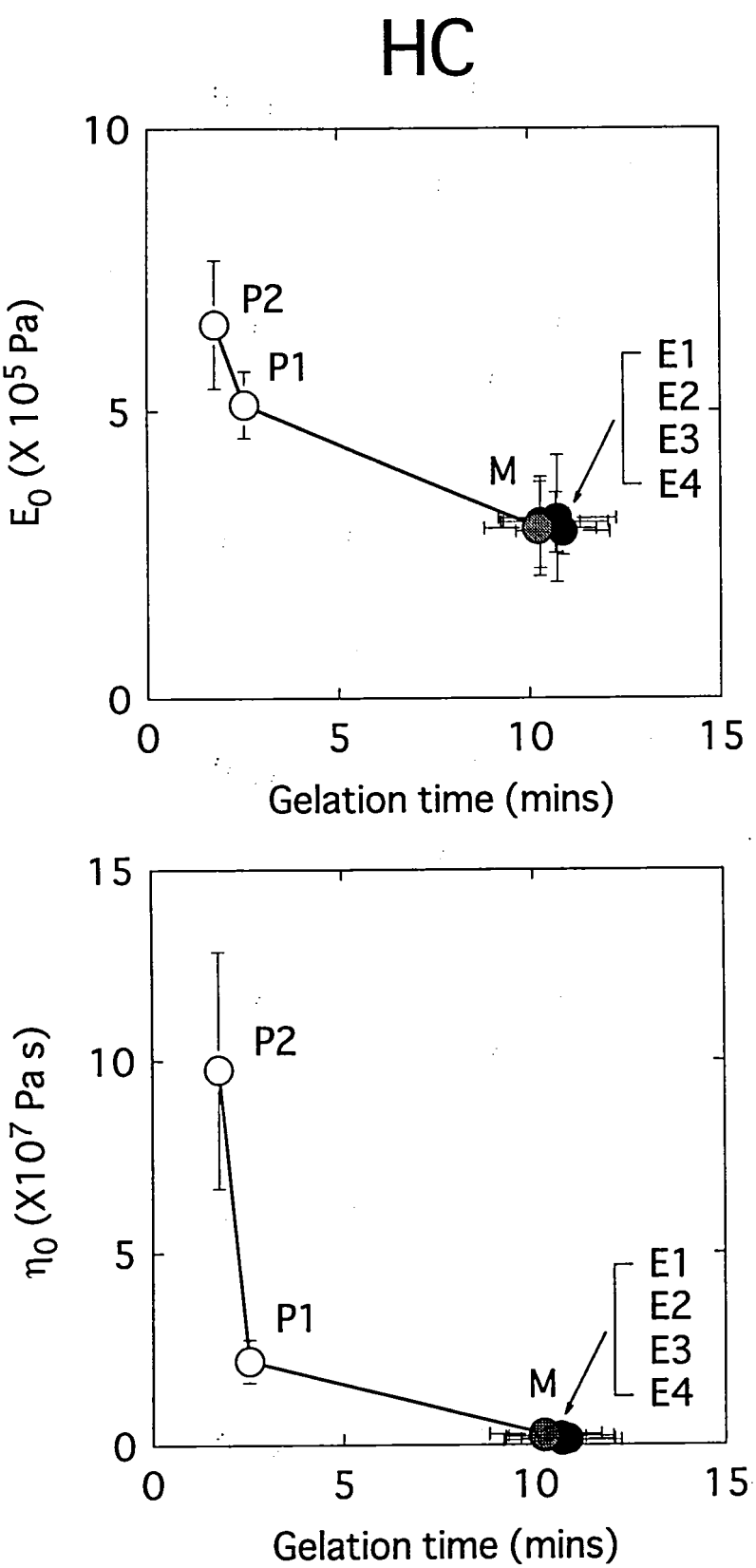
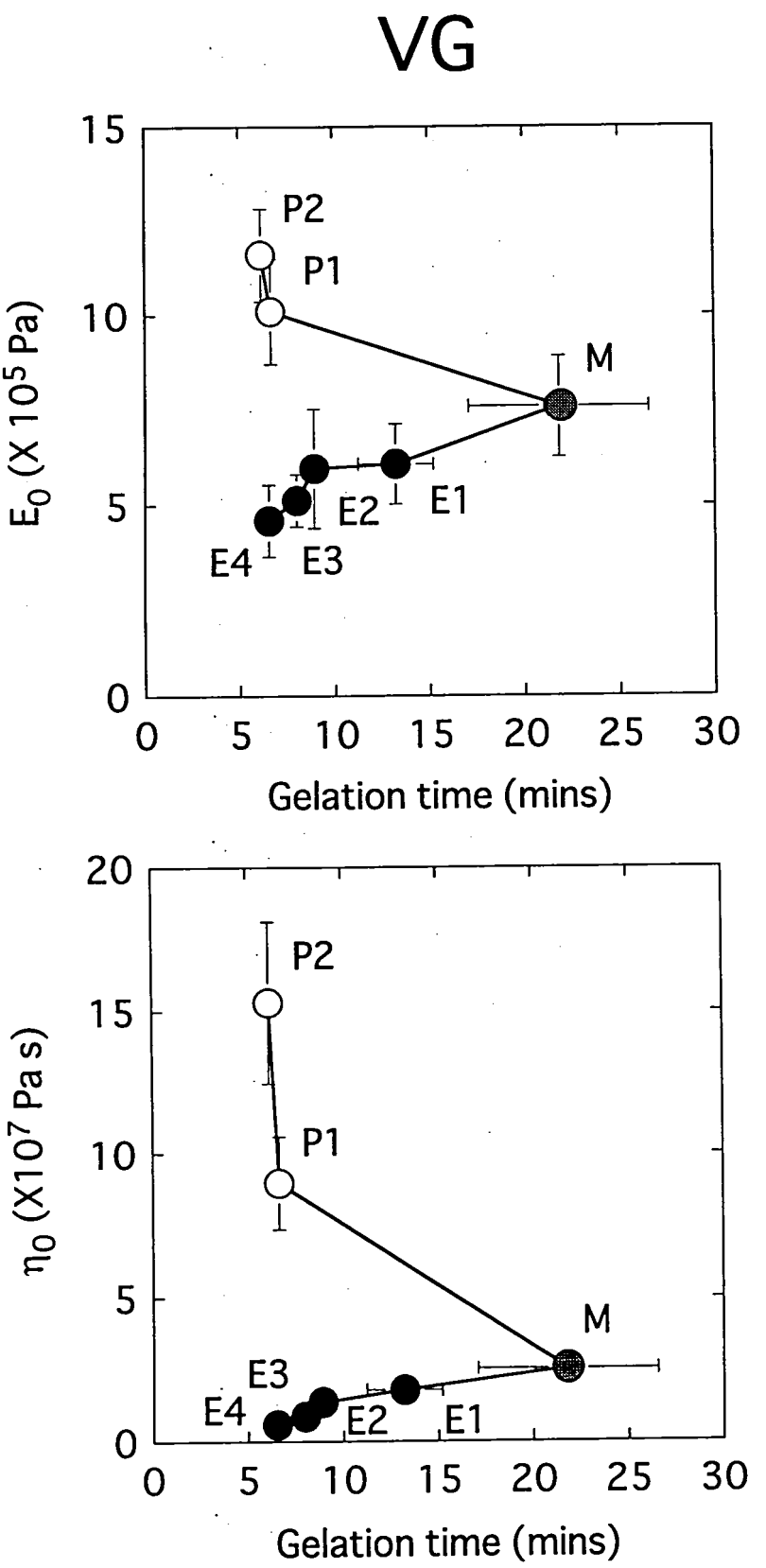

HC
10
5
0
0
5
10
15
E_0 (X 10^5 Pa)
P2
P1
M
E1
E2
E3
E4
Gelation time (mins)
15
10
5
0
0
5
10
15
η_0 (X10^7 Pa s)
P2
P1
M
E1
E2
E3
E4
Gelation time (mins)

Fig.9


VG
15
10
5
0
E_0 (X 10^5 Pa)
P2
P1
M
E1
E2
E3
E4
0
5
10
15
20
25
30
Gelation time (mins)
20
15
10
5
0
η_0 (X10^7 Pa s)
P2
P1
M
E3
E4
E2
E1
0
5
10
15
20
25
30
Gelation time (mins)