# The effect of blending on the rheological properties of gelatin solutions and gels

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The effect of blending on rheological properties for an acid and alkaline processed gelatin has been investigated. Blending of weak gels (1·0–3·5 % w/v at 25°), resulted in a decrease in gel rigidity whereas in the stronger gels (5–50 % w/v at 25°) and solutions (18 % and 30 % w/v at 35°), an increase occurred. The decrease in structure in the weak gels is considered to be due to coulombic effects, minimum strength occurring for a mixture which possessed zero charge in solution. A tentative explanation for effects in rigid gels and concentrated solutions is offered.

The relation between rigidity and concentration of gelatin gels has been studied extensively by Ferry (1948a). Similar studies with gelatins with widely differing molecular weights have been restricted to 5·73% gels. Ferry (1948a) found that the rigidity of a 50:50 mixture of gelatins was less than the arithmetic mean of the rigidities of the individual samples.

Hard gelatin capsules may be prepared from either acid or alkaline processed gelatins, or from blends of both, and we have therefore investigated the effect of blending on the rheological properties of such blends. In the present work, non-destructive creep compliance tests have been used to measure the viscoelastic properties of mixtures of acid and alkaline gelatin solutions (18% w/v at 35°) and gels (1·5%–3·5% w/v at 25°). Rigidities of the mixtures have been measured using a modified Saunders and Ward rigidiometer (Timson & Kelly, 1966), for the concentration range 5–50%. Continuous shear experiments were performed on 30% w/v solutions over the temperature range 30°–50°.

## MATERIALS AND METHODS

### Materials

The gelatins were commercial acid and lime processed ossein samples (Croda Ltd.) suitable for use in hard gelatin capsule manufacture. The properties and physical characterization of these samples has been reported previously (Robinson, Kellaway & Marriott, 1975).

### Methods

1·5–3·5% w/v gels and 18% w/v solutions were prepared and maintained at 50° for 1 h and then at 4° for 21 h. The gels, having been equilibrated at 25° for 2 h, were loaded between the cone and plate of an air turbine viscometer (Marriott, Irons & Harris, 1973) and equilibrated for a further 1 h at 25° in a saturated atmosphere. The 18% w/v solutions were equilibrated at 35° for 2 h, loaded between the cone and plate, and equilibrated for a further 1 h at 35° in a saturated atmosphere. Results were subjected to a line spectra analysis similar to that described by Warburton

& Barry (1968), and a computer program was written for this procedure. Gels in the higher concentration range (5–50%) were prepared and maintained at 50° for 1 h, poured into the rigidiometer tubes, allowed to cool to 4° and aged for 21 h. The gels were equilibrated at 25° for 30 min and rigidities were then determined. 30% w/v solutions were prepared and maintained at 50° for 1 h, poured into the cup of an Epprecht Rheomat 30 viscometer (Contraves Ltd., Zurich), and allowed to equilibrate at the required temperature for 30 min. Rheograms were obtained directly using the Rheomat 30 in conjunction with a Rheoscan programming unit and an XY recorder (Farnell Instruments, Wetherby). A sweep time of 2 min and a maximum shear rate of 195 s$^{-1}$ were used.

The effect of blending in dilute solution was investigated for 0·2% w/v aqueous gelatin solutions at 25° by U-tube viscometry and turbidity measurements. In addition, electrophoretic mobility measurements were carried out in a microelectrophoresis apparatus (Rank Bros., Bottisham, Cambridge), using a capillary cell. Conductivities were determined using a conductivity bridge and 'dipcell' (Autobalance Universal B642, Wayne-Kerr Instruments, Bognor Regis), and pH was measured using a combined pH—calomel electrode pair (Corning-EEL Activion electrode in conjunction with a Corning pH meter, model 113, Corning-EEL, Halstead, Essex). The gelatin mixtures were adsorbed onto polyvinyltoluene (PVT) latex spheres 1·87 $\mu$m diameter, 10$^5$ particles ml$^{-1}$ for the electrophoretic mobility determinations. The final gelatin concentration was 0·05% w/v.

Blended gels (2·5% w/v) were prepared and maintained at 4° for 1 h, equilibrated as gels at 25°, or sols at 30°, for 1 h and the pH determined.

### RESULTS AND DISCUSSION

The effect of concentration over the range 1·0–3·5% w/v on the instantaneous shear compliance, (J$_0$), and the steady state shear viscosity, ($\eta_0$), is shown in Fig. 1. The observed fall in compliance and corresponding rise in viscosity with increasing
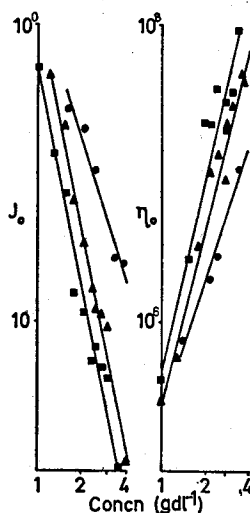


FIG. 1. The effect of concentration on the instantaneous shear compliance, J$_0$ (m$^2$ N$^{-1}$) and the steady state shear viscosity $\eta_0$ (Ns m$^{-2}$) of gelatin gels at 25°. ■ Alkaline gelatin. ▲ Acid gelatin. ● 50:50 blend.

concentration are considered to be indicative of an increase in gel network. The compliance of the 50:50 blend was higher and the viscosity lower at all concentrations examined compared with the individual acid and alkaline samples, indicating a less rigid gel structure. It is apparent that the slopes of both $J_0$ and $\eta_0$ against concentration plots for the acid and alkaline gels are approximately parallel. The slopes of $J_0$ against concentration for the acid and alkaline gelatins were $-5.0$ and $-4.6$ respectively. In contrast the value for the slope of the 50:50 mixture was $-2.99$ which is perhaps indicative of some network differences in the blends. Similarly, the slopes of $\eta_0$ against concentration for acid, alkaline, and 50:50 blends were $4.0$, $4.5$ and $2.8$ respectively. The blends appeared cloudy and opalescent, exhibiting light scattering, which may perhaps be attributed to extensive particle-particle interaction. The more rigid nature of the alkaline gel compared with the acid sample has been discussed previously (Robinson & others, 1975).

Fig. 2 shows the effect of blending on reduced viscosity, $\eta_{red}$, and on turbidity. In both cases the shape of the curves was similar and a minimum was observed between 25 and 30% alkaline, 70–75% acid gelatin which may be attributed to coulombic effects, the positive charge on the acid gelatin being neutralized by the negative charge of the alkaline sample.
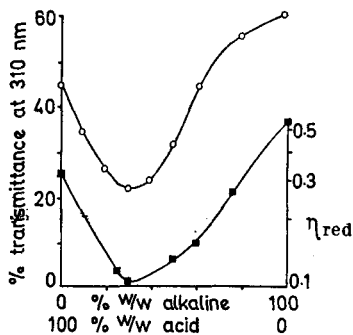


FIG. 2.   The effect of blending acid and alkaline gelatin solutions (0.2% w/v at 25°) on reduced viscosity ■ and turbidity ○.

The effect of blending on conductivity and pH for 0.2% w/v sols and 2.5% w/v gels is shown in Fig. 3. Although the conductivity increased on blending, a plateau was apparent over a wide range of blends indicating release of bound ions. A minimum in pH occurred at a ratio which corresponded to the minimum observed for the viscosity and turbidity data. It is apparent that hydrogen ions were released in blends containing high proportions of acid gelatin although this does not entirely account for the differences detected by conductivity measurements. The pH of 2.5% w/v sols and gels (5.55) was unaffected by blending and the decrease in rigidity noted for blended 2.5% w/v gels (Fig. 5) cannot be attributed to changes in hydrogen ion activity. This is supported by the work of Gerngross (1926), Ferry (1948b) and Cumper & Alexander (1952) when gel rigidity was shown to be constant over the pH range 4–10.

Fig. 4 shows the effect of blending on the electrophoretic mobility of gelatin mixtures adsorbed on to PVT latex. The isoelectric blend occurred at about 25% alkaline 75% acid gelatin which corresponded to the minima observed for the
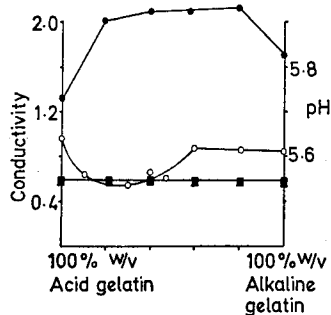
FIG. 3. The effect of blending 0·2% w/v acid and alkaline gelatin solutions on conductivity ($\Omega$ m$^{-1}$ g$^{-1}$ litre $\times$ 10$^{-1}$) and pH and the effect of blending 2·5% w/v solutions and gels on pH. ● Conductivity measurements (0·2% w/v solutions). ○ pH measurements (0·2% w/v solutions). ■ pH measurements (2·5% w/v gels at 25°). ▲ pH measurements (2·5% w/v gels at 30°).

viscosity and turbidity (Fig. 2). The pure acid sample possessed a considerably lower mobility ($+0·168$ $\mu$m s$^{-1}$ V$^{-1}$ cm) than the alkaline sample ($-0·815$ $\mu$m s$^{-1}$ V$^{-1}$ cm).

Fig. 5 shows the effect of blending on $J_0$ and $\eta_0$ for 2·5% w/v gels. A maximum compliance was observed in the 50:50 blend and a minimum viscosity at about 60:40 alkaline:acid, indicative of less rigid gel networks for the blends. The maximum and minimum did not coincide with the isoelectric mixture and it is possible that some other interaction was taking place producing the observed shift. The mobility, turbidity, and viscometric determinations were carried out in dilute solutions (0·2 and 0·05%) whereas the gels contained 2·5% gelatin. Since the decrease in rigidity did not seem to be entirely due to charge effects it was decided to investigate blending in more concentrated solutions and more rigid gels.

The effect of blending on more rigid gels (5–50% w/v) is shown in Fig. 6. It can be seen that maxima occurred in the rigidity-concentration plots between 40–50 alkaline:acid blends and this increase in rigidity modulus, G, was some fifteen fold for the 50% w/v gels. The increase in G may be due to an increase in entanglements, interactions between end groups, a greater degree of cross-linking, or incorporation of the lower molecular weight acid gelatin chains into the gel interstices of the higher molecular weight alkaline chains, giving rise to a 'filling' effect.

Table 1 shows the effect of concentration on rigidity modulus. When log c is plotted against log G then a linear relation is produced ($P > 0·001$).

The relation is given by equation 1.

$$\log G = n \log c + k \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (1)$$

where n and k are the slope and intercept and

$$G = kc^n \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (2)$$

Table 1. *The effect of gelatin concentration on the Rigidity modulus, G, according to the relation log G = n log c + k.*

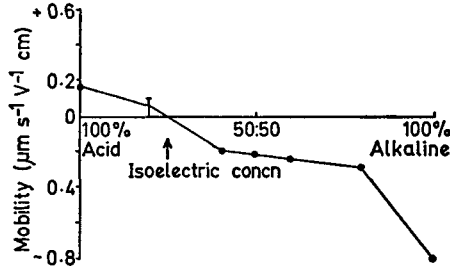| Gelatin type | Slope (n) | Intercept (k) | *P* |
|---|---|---|---|
| Acid | 1·266 | 2·99 | >0·001 |
| Alk. | 1·682 | 2·74 | >0·001 |
| 50:50 blend | 1·985 | 2·34 | >0·001 |

FIG. 4. The effect of blending on the electrophoretic mobility of gelatins adsorbed on to PVT-latex at 25°.

The gelatins used in this work were not found to obey the relation given in equation 3,

$$G \propto \sqrt{c} \quad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (3)$$

which was reported by Leick (1904). Sheppard & Sweet (1921) were able to show the relation given in equation 4.

$$G \propto n\sqrt{c} \quad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (4)$$

where $n < 2$.

Other workers, Sauer & Kinkel (1925), Poole (1925), Ferry (1948a), Cumper & Alexander (1952), Hirai & Kishimoto (1953), have reported conflicting results. It has been shown that G is related to the square of the gelatin concentration for some samples but not for others. The deviations occurring for the same gelatin have been shown to be dependent on the temperature of measurement, concentration range, and degree of thermal degradation. Miller, Ferry & others (1951) proposed the relation

$$\sqrt{G}_{blend} = \frac{(\sqrt{G_1} + \sqrt{G_2})}{2} \quad .. \qquad .. \qquad .. \qquad .. \qquad (5)$$

for a 50 : 50 mixture of two degraded ossein gels. However, the gelatins studied in this work did not obey the above relation. It is unlikely that a simple relation exists for all gelatins although the square law has formed a satisfactory basis for the general industrial blending of gelatins.

For the derived relations (Table 1), the exponent 'n' increases in the order acid, alkaline, 50 : 50 blend and thus for a given concentration the order of increasing rigidity would be acid, alkaline, 50 : 50 blend.
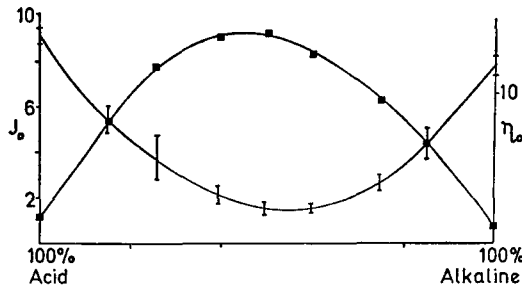


FIG. 5. The effect of blending for 2·5% w/v gelatin gels on the instantaneous shear compliance, $J_0$ ($\times 10^2$ m$^2$ N$^{-1}$) and the steady state viscosity, $\eta_0$ ($\times 10^{-5}$ Ns m$^{-2}$) at 25°. ■ Instantaneous shear compliance. Barred curve—steady state shear viscosity.
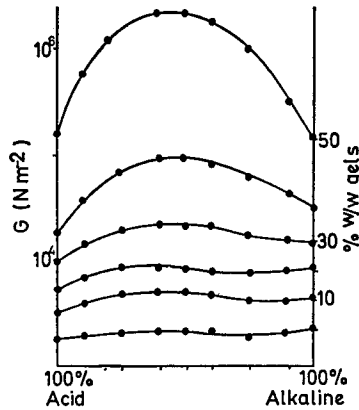
FIG. 6.  Rigidity of blended acid and alkaline gels at 25°.

Fig. 7 shows the effect of blending on $J_0$ and $\eta_0$ in 18% solutions at 35°.  A minimum compliance and a maximum viscosity were observed between 25–50% alkaline: acid indicative of a greater degree of structure in these viscous blends, supporting the results obtained for the rigidity modulus (Fig. 6).   Similar results were obtained for $J_1$ and $\eta_1$ (Fig. 8), the compliance and viscosity of the first Voigt unit respectively.

Viscosity data from continuous shear experiments performed on 30% solutions over the range 35°–50° are shown in Table 2.   In other than at 35° cases the order of increasing viscosity is acid, 50:50 mixture, alkaline.   However, the viscosity of the mixture is greater than the arithmetic mean of the individual samples which is in agreement with the results for two gelatins, reported by Ferry (1948a).   At 35° the

Table 2.  *The effect of temperature on 30% w/v acid and alkaline gelatin solutions.*

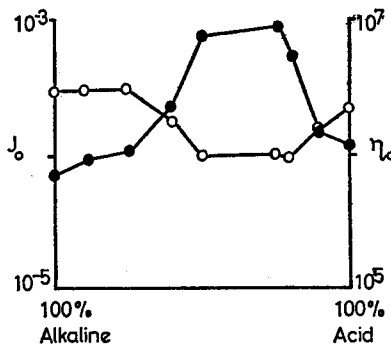| T°C | Viscosity of gelation solutions (Ns m⁻²) | | | |
| | Acid | Alkaline | 50:50 | Arithmetic mean |
| --- | --- | --- | --- | --- |
| 35 | Complex anticlockwise rheograms. | | 50:50> Alk > acid | |
| 40·5 | 1·56 | 2·94 | 2·35 | 2·25 |
| 45·4 | 1·12 | 2·03 | 1·88 | 1·57 |
| 50 | 1·03 | 1·84 | 1·75 | 1·43 |



FIG. 7.  The effect of blending 18% w/v gelatin solutions on the instantaneous shear compliance, $J_0$ (m² N⁻¹) and the steady state viscosity, $\eta_0$ (Ns m⁻²) at 35°.  ● Instantaneous shear compliance. ○ Steady state shear viscosity.
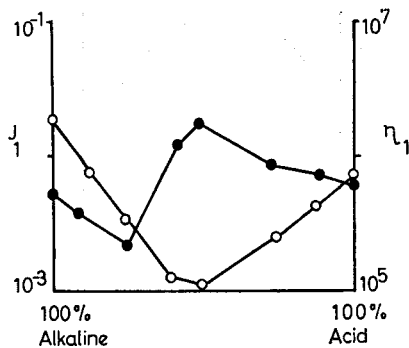
FIG. 8. The effect of blending 18% w/v gelatin solutions on the retarded compliance of the first Voigt unit ($J_1$) and viscosity ($\eta_1$) at 35°. ● Retarded compliance of the first Voigt unit ($J_1$) ○ Viscosity of first Voigt unit ($\eta_1$). Units as in Fig. 7.

solutions exhibited complex anticlockwise rheograms and evidence of the Weissenberg effect was apparent. The order of increasing viscosity and structure build up was acid < alkaline < 50:50 mixture. Interactions were indicated in the 50:50 mixtures which became more evident as the temperature of measurement decreased and gelation occurred.

From the results presented it would appear that blending of weak gels resulted in a decrease in gel rigidity whereas in the stronger gels and solutions at 35° an increase occurred.

The decrease in structure in the weak gels may be attributed to coulombic effects, minimum strength occurring for a mixture which possessed zero charge in solution. An opposite effect was observed for the stronger gels and for the 18% w/v solutions.

It is obviously important to be aware of changes which may occur when gelatins are blended since alterations in the mechanical properties of the final product may occur. Also, in hard gelatin capsule manufacture, the thickness of the capsule wall and uniformity of shape will be dependent on the rheological properties of the gelatin systems used.

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