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Mechanical Spectroscopy of Filled Gelatin Gels

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SUMMARY

Small deformation mechanical measurements were performed on the model system of glass filled gelatin gels. By using well characterised samples of glass spheres, rods and irregular pieces of intermediate shape, e.g. plates at varying phase volume of filler, the effect of size, shape and phase volume on the shear storage and loss moduli could be investigated.

INTRODUCTION

The effect of particle shape on the mechanical properties of filled polymers has been extensively investigated theoretically, and a number of recent reviews have appeared (NIELSEN 1974; MANSON AND SPERLING 1976; LIPATOV 1977; DICKIE 1979; CHOW 1980) which discuss the various mechanical models used in such treatments. However there is a surprising paucity of reliable experimental data which relate, for example, the effect of phase volume, particle size, and shape of filler phase to the properties of the polymer composite for other than the two extremes, viz. spherical and rod shaped particles. We describe a series of experiments in which glass particles of well characterised size and shape were dispersed in a gelatin sol, and the resultant gelled composite studied under a range of conditions, as ϕ the phase volume of glass was varied. The glass particles were size and shape sorted into rods, plates, 'cubes' and spheres. The small deformation shear moduli, G' and G'' were measured using the Rheometrics Mechanical Spectrometer and results discussed in terms of the effect of size and shape of filler particles, and ϕ on both G' and the viscoelastic damping factor, $\tan\delta$ (= G''/G').

EFFECT OF PHASE VOLUME ON MODULUS

The simplest treatment of the effect of filler on the moduli of a composite is analogous to the classical Einstein viscosity equation so that

$$G_c/G_0 \; = \; 1 + a\phi + b\phi^2 + \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

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where G_c is the modulus of composite, G_o that of matrix, ϕ the phase volume of filler, and a and b are coefficients which depend, e.g. on the shape of filler particles and their degree of agglomeration (NIELSEN 1979). ϕ_m is the 'maximum packing fraction' which the system can maintain as a filler phase. A variety of other expressions have been proposed to relate G_c/G_o to ϕ, but most are designed for spherical particles. Those treatments which have been most widely accepted are those due to VAN DER POEL (1958) (simplified by SMITH; 1975), and by KERNER 1956. In this work we use the van der Poel approach, which although not given explicitly, is charted in fig. 2.

EXPERIMENTAL

Materials

Gelatin was supplied in granular form as a gift from Leiner Ltd., Treforest, Glamorgan, U.K. The nominal Bloom strength was 300 (high primary chain M_w), and solutions were made up in warm distilled water (60C) at 25% w/w. Earlier experiments had indicated that at lower gelatin concentration, the warm solution was not sufficiently viscous to disperse the glass evenly up to the time of gelation. The density of the gelatin gel after allowing for partial shrinkage (~90 mins at 25C) was 1.069 (± 0.003) gm ml^{-1}. Glass microspheres supplied as ballotini by Jencons Scientific Ltd., were obtained in two sizes - nominally Grade 20 (mean diameter ~40μ) and Grade 15 (~80μ). Glass rods were obtained by loosely cutting glass wool, mixing as a slurry with chloroform, and passing through a hammer mill 3 or 4 times. The fragments were dried and size fractionated by passing down sucrose density columns. In this way 3 reasonably discrete 'middle' fractions were obtained. Particle sizing indicated that the mean length $\bar{l}$ of these were 108, 144 and 244μ respectively. To obtain more irregular shapes, ballotini fragments were shape sorted using the table at the School of Pharmacy, University of London (Dr. K. Ridgway). The irregular flat pieces were designated plates, and the more 3-D fragments, although of irregular shape were designated 'cubes'. The density of the ballotini were found to be 2.9 ± 0.05, that of the glass wool lower at 2.5 ± 0.05. Around 1. - 1.5 mls of each filled gelatin gel was prepared by slowly stirring the correct weight of glass into the gelatin solution maintained at 60C, until all had been added. In practice it was found that by this method it was quite easy to estimate ϕ_m. For example with the 144μ rods, a specimen with ϕ = 0.265 behaved as an extremely viscous liquid, whereas one with ϕ = 0.275 had no coherence, and when gelled was found to be of substantially lower modulus.

Mechanical Measurements

The gelatin sol plus filler was introduced between the pre-warmed parallel plates of the Rheometrics and the sample cooled to 25C ($\simeq$ 20 min). During this time, and for the next 90 mins, G'' and G', the dynamic loss and storage moduli were charted every minute. During the gelation, the oscillatory frequency was 10 rad sec^{-1}, and the shear strain γ was low (typically 0.5 - 10% - lowest value corresponding to $\phi \sim \phi_m$). After this time a frequency sweep (10^{-2} to 10^{+2} rad sec^{-1}) and usually a strain sweep (.2% - 10%) were performed to ensure that measurements had been made in the linear viscoelastic region.

RESULTS AND DISCUSSION

Frequency Sweeps

Figs 1A and B contrast the frequency response for an unfilled and a filled gel. G' is almost independent of frequency for both. Measurements of G'' for the unfilled gel show a shallow minimum centered ~1 rad sec^{-1}. As the amount of filler is increased, the minimum becomes even less pronounced, and begins to shift to lower frequencies. In general, the effect of filler on tan δ depends upon the nature of the matrix: it may increase if the matrix is rubbery, or decrease if the matrix is glassy (MANSON AND SPERLING 1976). In this work only the former case is observed, presumably as additional dampening mechanisms occur such as filler-matrix function, which can result in dissipation of energy (LEWIS AND NIELSEN 1970).

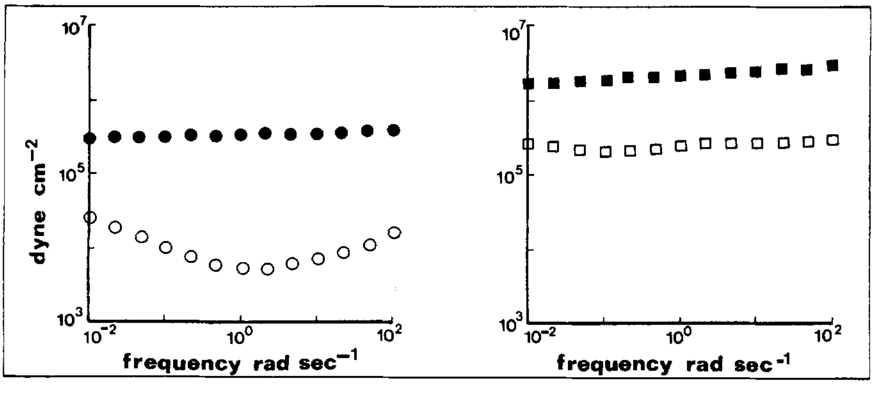

Fig. 1(A) G', G'' for unfilled gel, vs. frequency

Fig. 1(B); as 1(A) - filled gel; ϕ = 0.489 spheres grade 20.

Because of the comparative 'flatness' of the frequency response, in succeeding sections we will discuss only results corresponding to ω = 10 rad sec^{-1}. Replicate experiments gave G_0 (= G'(10) for unfilled gel) as 3.57 and 3.47 x 10^5 dyne cm^{-2}.

Spheres and Rods

For $\phi > \phi_m$, G_c/G_0 falls well below the theoretical line (arrowed point). The data for rods includes those of mean length, $\bar{l}$, 108, 144 and 244μ. Overall ϕ_m for rods was ≈0.27, and depends only slightly upon $\bar{l}$ - thus for those with $\bar{l}$ of 108μ, $\phi_m \approx 0.28$.; $\bar{l} = 144\mu$, $\phi_m \approx 0.27$.

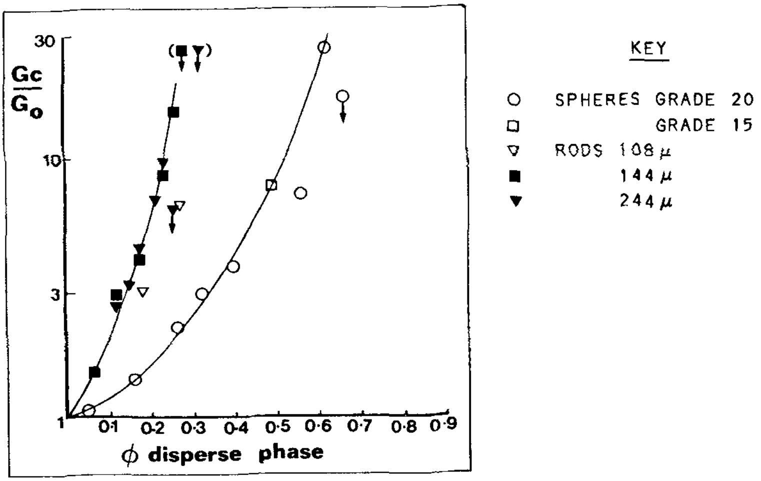

Fig. 2. G_c/G_0 plotted against volume fraction filler for glass rods and spheres. A black arrow indicates $\phi > \phi_m$. Bracketed data points could not be measured. The line for spheres is that of van der Poel, that for the rods is an empirical fit.

Plates and Cubes

For these particles, both size and 'shape' represent relatively crude averages. Overall, however, the data are encouraging with G_c/G_0 at the same ϕ falling in the expected order viz. rods > plates > 'cubes' > spheres; ϕ_m for plates ≈ 0.41 and for 'cubes' ≈ 0.54. Because of the small amounts of sample which could be sorted and characterised, only one measurement was made to examine size effects. However, this point (corresponding to the 90 - 125μ plates) falls on the same line as for the smaller (63-90μ) plates, supporting the consensus of results from the spheres and rods viz., that size and size distributions effects were not very significant compared to the 'shape' effect. Large deformation measurements have indicated that size effects can change, for example, the fracture toughness (TRACHTE AND DIBENEDETTO 1971). The shape effect appears to change G_c/G_0 only through its influence on ϕ_m.

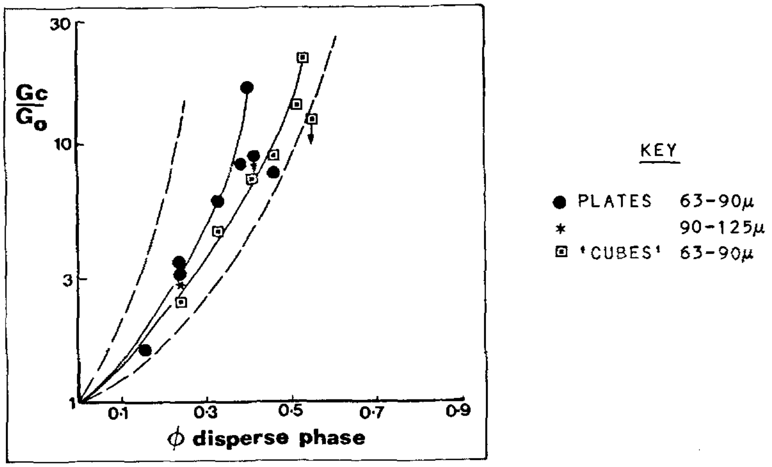

Fig. 3. As fig. 2, but for cubes and plates.

In fig. 4, all the data is plotted against the reduced packing fraction ϕ/ϕ_m. The solid line is that of van der Poel rescaled to $\phi_m \simeq 0.68$, the dotted line is due to LANDEL 1958, again designed for spheres but here used for all shapes of particle, viz. $G_c/G_o = (1 - \phi/\phi_m)^{-5/2}$. The data tend to lie between these estimates, but generally fall below the van der Poel line for $\phi/\phi_m > 0.9$.

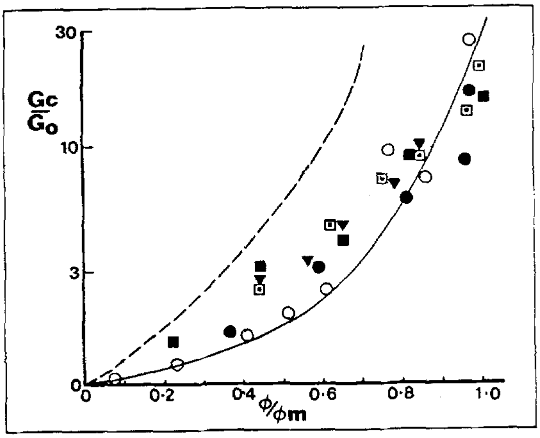

Fig. 4. G_c/G_o plotted agains ϕ/ϕ_m. Symbols as in figs. (2) and (3).

The loss tangent, $\tan\delta$, is a measure of the ratio of energy lost to energy stored in cyclic deformation; $\tan\delta$ increases as ϕ increases cf. fig. 5., and, although somewhat scattered, this increase is similar to that in fig. 2., with the greatest effect for rods, and the smallest for the spheres. Even the ratio of $\tan\delta$ for filled and unfilled gels is the same order as that found for G_c/G_o.

Further tan δ seems to be a more sensitive probe of the size effect (cf. the data for rods) than is the modulus ratio. However, since the properties of a composite may be drastically modified by, e.g. surface treatment of the filler to improve adhesion (SAMU AND BROUTMAN 1972), any detailed argument about the mechanism of this effect must be treated with caution.

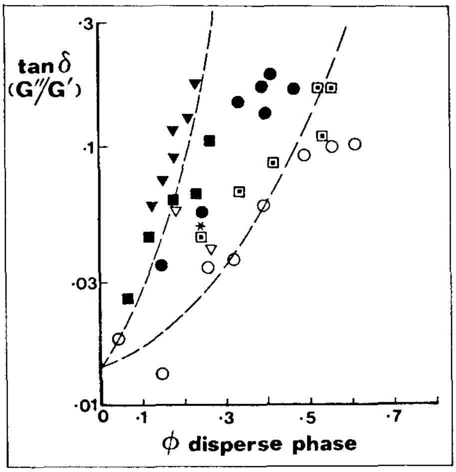

Fig. 5. tan δ plotted against ϕ; dotted lines and symbols as figs. 2 and 3.

CONCLUSION

This work has investigated, using well characterised filler particles, the effect of particle shape, size and volume fraction on the properties of a gelatin composite. Whilst the method appears suitable for small deformation measurements, the difficulty in preparing large samples of filler by the present methods limits the applicability for the measurement of ultimate properties.

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