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THE RHEOLOGICAL PROPERTIES OF CARBOPOL GELS II. OSCILLATORY PROPERTIES OF CARBOPOL GELS

B.W. BARRY and M.C. MEYER

School of Pharmacy, University of Bradford, Bradford, West Yorkshire BD7 1DP and School of Pharmacy, Portsmouth Polytechnic, Portsmouth PO1 2DZ (England)

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SUMMARY

Viscoelastic properties of aqueous Carbopol gels were examined at frequencies of 7.91 × 10^{-3} to 25 Hz using a Weissenberg rheogoniometer. Neutralized gels changed little from 10 to 50°C and were similar to unneutralized gels. Data confirmed the dominant elastic nature of Carbopol gels (phase lags of 2–14°) and the relative small change of the storage modulus with frequency indicated that the polymer was strongly entangled and the gels were examined in their plateau region of viscoelastic behaviour. Some correlation of oscillatory data with continuous shear properties was observed.

Oscillatory data obtained at different temperatures were combined with creep data using the method of reduced variables; satisfactory composite curves over a slightly increased frequency range were obtained. When creep data were transformed into dynamic data and combined with experimental oscillatory results, using exact viscoelastic relationships, curves were obtained which described the behaviour of Carbopol gels over seven frequency decades. From this behaviour it was suggested that Carbopols were high molecular weight amorphous polymers with long side chains. The practical aspects of the transformation procedure were discussed and it was shown that neither small strain technique alone covered the entire frequency or time range necessary for an exhaustive study of Carbopol gels.

INTRODUCTION

Carbopols are a group of carboxyvinyl polymers cross-linked with allyl sucrose. These polymers are widely used in the pharmaceutical and cosmetic industries and yet little is known about their fundamental viscoelastic properties. Recently, continuous shear and creep techniques were used to investigate the rheological properties of Carbopol gels (Barry and Meyer, 1978). However, these methods have certain disadvantages. Continuous shear tests are quick to perform but do not provide fundamental data and creep tests are restricted by the response time of the apparatus and recording system and by the difficulty of applying an instantaneous stress at the beginning of each experiment. In order to supplement such transient experiments Carbopol gels were examined by oscillatory testing. Dynamic tests provide information corresponding to short times, as a periodic experiment at a frequency of ω rad s^{-1} is qualitatively equivalent to a transient experiment at time $t = 1/\omega$ s.

For an exhaustive study of semisolids it is necessary to use both transient and dynamic experiments because neither method alone determines viscoelastic properties over a sufficiently broad time or frequency range. Although data from each type of experiment are generally not directly comparable, fundamental parameters may be mathematically converted using linear viscoelastic theory to provide a unified parameter applicable at both high and low frequencies.

Various formulae are available for the calculation of the storage and loss compliances ($J'(\omega)$ and $J''(\omega)$ respectively) from the total creep compliance ($J(t)$ where $t = 1/\omega$). Ferry (1970) derived exact equations for the conversion of transient data to dynamic data based on linear viscoelastic theory for the Maxwell and Voigt models. The same author described other equations that can be used to unify data obtained at different temperatures by combining the residual viscosity (η_0) with the storage and loss compliances (method of reduced variables). The data required for these conversions may be obtained from a discrete spectral analysis of creep curves and both techniques are investigated here.

In this work a Weissenberg rheogoniometer was used in conjunction with a mechanical reference synchronizer and digital transfer function analyzer to investigate the dynamic rheological properties of Carbopol gels. The effects of polymer concentration, neutralization and temperature were studied.

Creep data obtained in previous work (Barry and Meyer, 1978) were transformed into dynamic functions in order to determine the feasibility of the conversion process and to assess the accuracy of the derived data with respect to the variables involved in creep and oscillatory experiments.

MATERIALS AND METHODS

Carbopol 940 and 941 [1] were stored over phosphorus pentoxide. Triethanolamine [2] B.P.C. was used as the neutralizing agent and water, freshly distilled from an all glass still, was the solvent.

A 1–10% range of gels was prepared in a standard manner by dispersing the required weight of polymer in water, followed by neutralization where applicable (Barry and Meyer, 1979). Air was removed by centrifugation. Gels were stored at 25 ± 1°C and tested between 3 and 8 days after preparation.

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[1] Honeywill Stein Ltd., London.

[2] B.D.H., Poole, Dorset.

Instrumental rheology

The behaviour of Carbopol gels in forced oscillation was investigated at 25 ± 0.1°C, between parallel plates (3.75 cm radius), sample gap width, 0.050 cm. Torsion bar constant was 1.030×10^7 dyne cm rad^{-1}. Approximate tests for linearity were performed by increasing the amplitude of oscillation from $\pm 7.7 \times 10^{-4}$ to $\pm 77 \times 10^{-4}$ rad at 2.5 Hz and deriving the amplitude ratio and phase lag from the experimental data. Departure from linearity was identified by an abrupt change in these results. Systems were then examined well within their linear viscoelastic region at frequencies of 7.91×10^{-3} to 25 Hz and values of amplitude ratio and phase lag were determined. These were used to calculate the storage modulus (G') and the dynamic viscosity (η') using the equations for parallel plate geometry derived by Walters (1968). Other viscoelastic functions were calculated from G' and η' using the following equations (Ferry, 1970):

$$G'' = \eta'\omega \tag{1}$$

$$\eta'' = G'/\omega \tag{2}$$

$$J' = G'/(G'^2 + G''^2) \tag{3}$$

$$J'' = G''/(G'^2 + G''^2) \tag{4}$$

where G'' = loss modulus and η'' = imaginary viscosity.

Calculation of storage and loss compliance from creep parameters

Data used in these transformations were obtained from discrete spectral analysis of creep curves for neutralized Carbapol 940 and 941 gels (Barry and Meyer, 1979). 1% and 3% neutralized gels were examined at 10, 25 and 50°C in oscillation and results were combined with transient data, using the method of reduced variables, to unify data with regard to temperature and to expand the frequency scale over which data were available (Ferry, 1970). The frequency shift factor was determined using the equation:

$$a_T = \eta T_0 \rho_0 / \eta_0 T \rho \tag{5}$$

where η is the residual viscosity in creep (data from Barry and Meyer, 1978), T is the absolute temperature and ρ is the sample density. The symbols which are subscripted zero are the same parameters, but refer to the reference temperature which was 298°K. The temperature reduction of the storage and loss compliances, J' and J'' respectively, was obtained using the equations:

$$J'_p = J' T\rho / T_0 \rho_0 \tag{6}$$

$$J''_p = J'' T\rho / T_0 \rho_0 \tag{7}$$

The subscript p indicates a temperature reduced variable and J' and J'' were obtained using Eqns. 3 and 4.

Loss and storage compliances were calculated from creep compliance from:

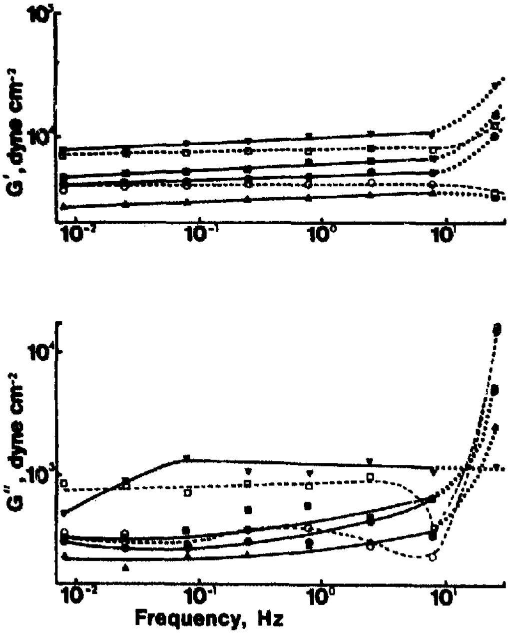
$$J'(\omega) = J_0 + \sum_{n=1}^{3} J_n/(1 + \omega^2 \tau_n^2) \tag{8}$$

$$J''(\omega) = \sum_{n=1}^{3} J_n\omega\tau_n/(1 + \omega^2\tau_n^2) + t/\eta_0 \tag{9}$$

where J_0 is the residual shear compliance in creep, J_1, J_2, J_3 are the shear compliances of the elastic parts of Voigt units 1, 2, 3 respectively, τ_1, τ_2, τ_3 are the retardation times of Voigt units 1, 2, 3, respectively and η_0 is the residual shear viscosity. Creep data for the 3% neutralized gels were selected for this conversion and combined with relevant data from oscillatory tests.

RESULTS

Results of linearity checks indicated that neutralized gels responded linearly over most of the amplitude range. At higher amplitudes (±60 X 10^{-4} rad) up to 10% variation in the derived parameters was observed for gels containing 5% polymer or less. Thus, to ensure that materials were examined in their linear viscoelastic region a relatively small amplitude of ±31 X 10^{-4} rad was used. Unneutralized systems did not show the same degree of



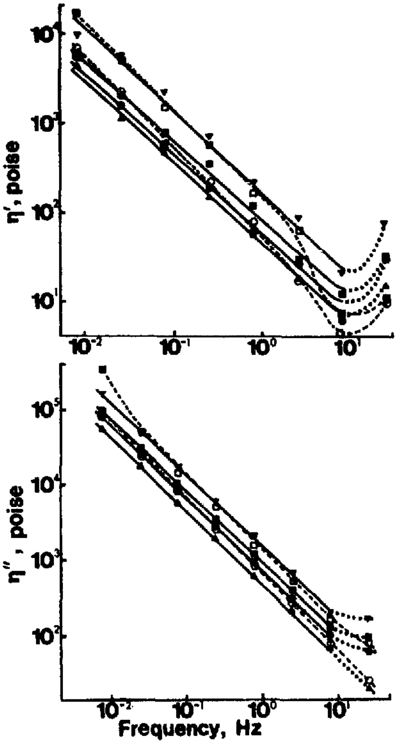


Fig. 1. Variation of G' and G'' with frequency for neutralized Carbopol 940 gels (solid lines and symbols) and unneutralized Carbopol 940 gels (dotted lines and open symbols). ▲: 1%; ●: 3%; ■: 5%; ▼: 10%; ○: 3%; □: 5%.

Fig. 2. Variation of η' and η'' with frequency for neutralized Carbopol 940 gels (solid lines and symbols) and unneutralized Carbopol 940 gels (dotted lines and open symbols). ▲; 1%; ●: 3%; ■: 5%; ▼: 10%; ○: 3%; □, 5%.

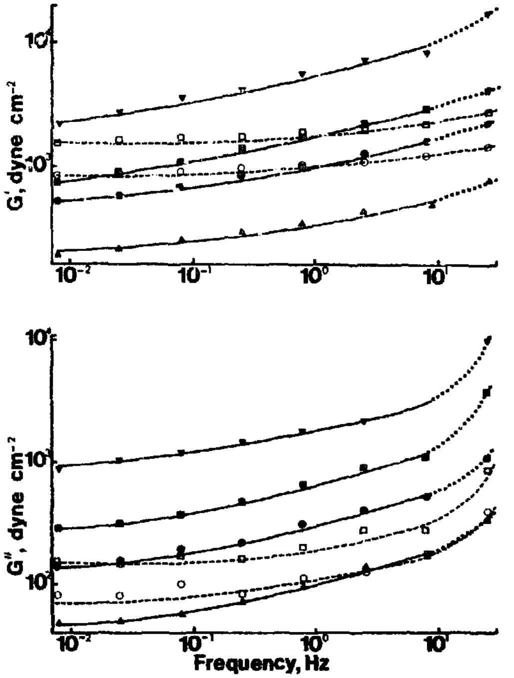


Fig. 3. Variation of G′ and G″ with frequency for neutralized Carbopol 941 gels (solid lines and symbols) and unneutralized Carbopol 941 gels (dotted lines and open symbols). ▲: 1%; ●: 3%; ■: 5%; ▼: 10%, ○: 3%; □: 5%.

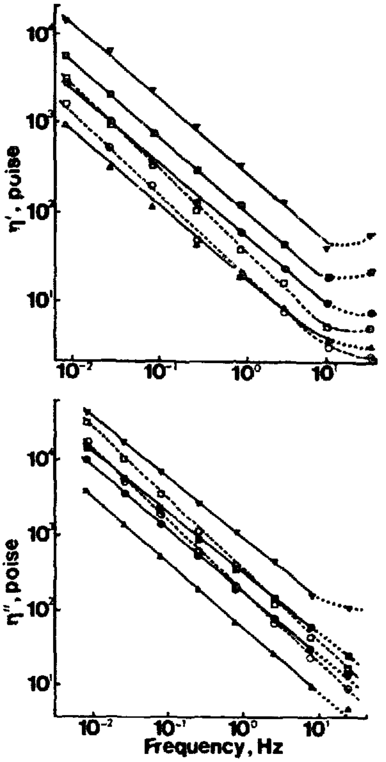


Fig. 4. Variation of η′ and η″ with frequency for neutralized Carbopol 941 gels (solid lines and symbols) and unneutralized Carbopol 941 gels (dotted lines and open symbols) ▲: 1%; ●: 3%; ■: 5%; ▼: 10%; ○: 3%; □: 5%.

linearity. 1% gels were non-linear throughout the amplitude range and were therefore not tested. 3% and 5% gels were linear up to an amplitude of approximately ±31 X 10^{-4} rad. Thus, these gels were tested at a lower amplitude, i.e. ±20 X 10^{-4} rad.

Neutralized Carbopol 940 gels behaved essentially as elastic bodies during the oscillatory tests. Phase lags were 2° or less even at a frequency of 7.91 X 10^{-3} Hz. Phase lags for unneutralized Carbopol 940 gels were marginally larger and amplitude ratios were slightly smaller than those obtained for similar neutralized systems. Neutralized Carbopol 941 gels exhibited a greater degree of viscoelasticity with phase lags ranging from 14° for 1% gels to 5° for 10% gels. Unneutralized Carbopol 941 gels exhibited smaller phase lags (2–4°) and higher amplitude ratios than comparable neutralized systems.

Variation of storage and loss modulus (G′ and G″), real and imaginary viscosity (η' and η'') and loss tangent ($\tan \phi = G''/G'$) with frequency for neutralized and unneutralized Carbopol gels are shown in Figs. 1–5. Effect of polymer concentration on G′, G″, η' and η'' is shown in Figs. 6 and 7.

Viscoelastic parameters derived from data obtained at different temperatures, although

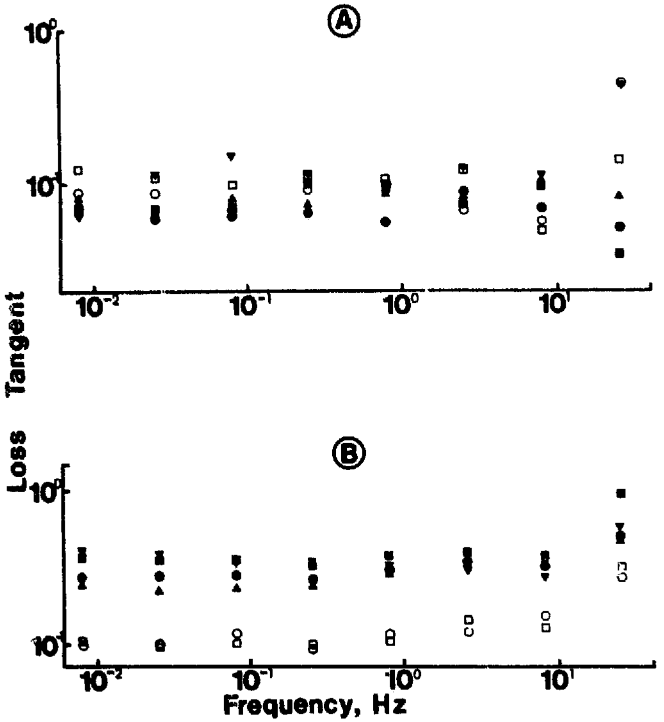


Fig. 5. Variation of loss tangent with frequency for neutralized (solid symbols) and unneutralized (open symbols) Carbopol 940 gels (A) and Carbopol 941 gels (B). To avoid confusion the data are not connected. ▲: 1%; ●: 3%; ■: 5%; ▼: 10%; ○: 3%; □: 5%.

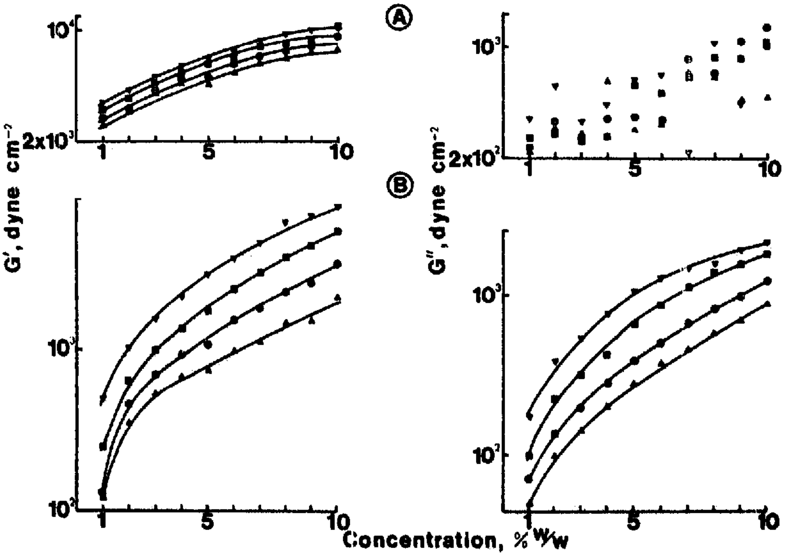


Fig. 6. Plots of G′ and G″ versus polymer concentration at several frequencies for neutralized Carbopol 940 gels (A) and neutralized Carbopol 941 gels (B). ▲; 7.91 × 10^{-3} Hz; ●: 7.91 × 10^{-2} Hz; ■: 7.91 × 10^{-1} Hz; ▼: 7.91 Hz.

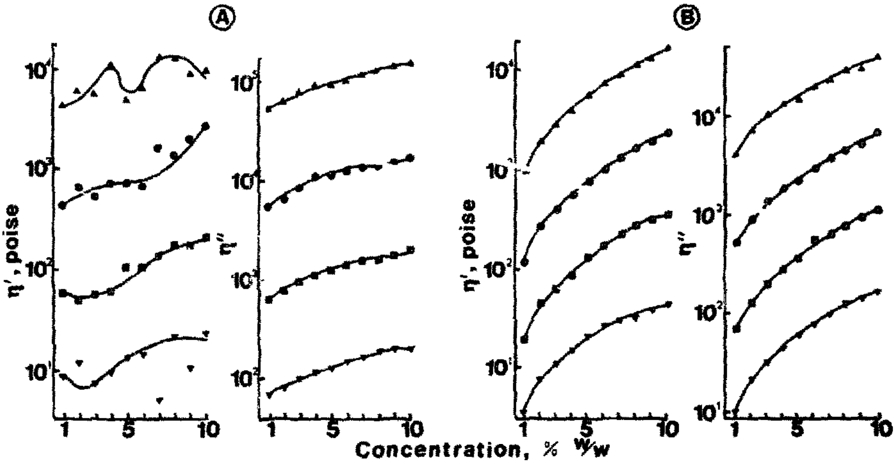


Fig. 7. Plots of η' and η'' versus polymer concentration at several frequencies for neutralized Carbopol 940 gels (A) and neutralized Carbopol 941 gels (B). ▲: 7.91×10^{-3} Hz; ●: 7.91×10^{-2} Hz; ■: 7.91×10^{-1} Hz; ▼: 7.91 Hz.

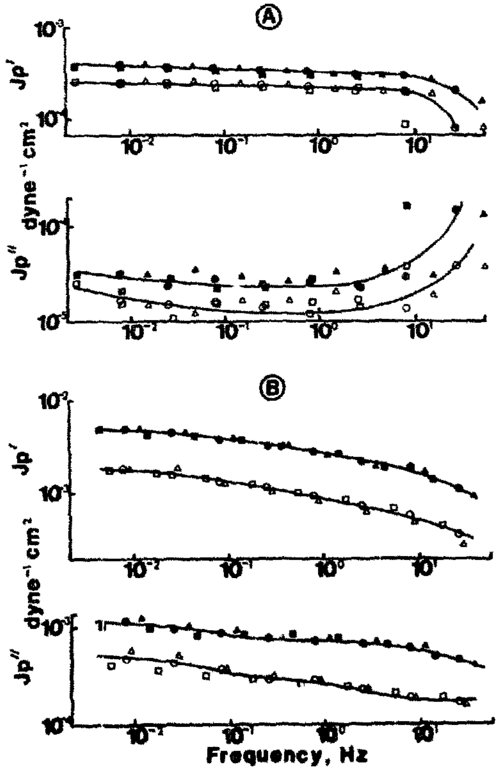


Fig. 8. Time-temperature equivalence plots for J′ and J″ for neutralized Carbopol 940 gels (A) and neutralized Carbopol 941 gels (B) obtained at 10°C (▲, △), 25°C (●, ○) and 50°C (■, □). Solid symbols indicate 1% gels and open symbols indicate 3% gels.

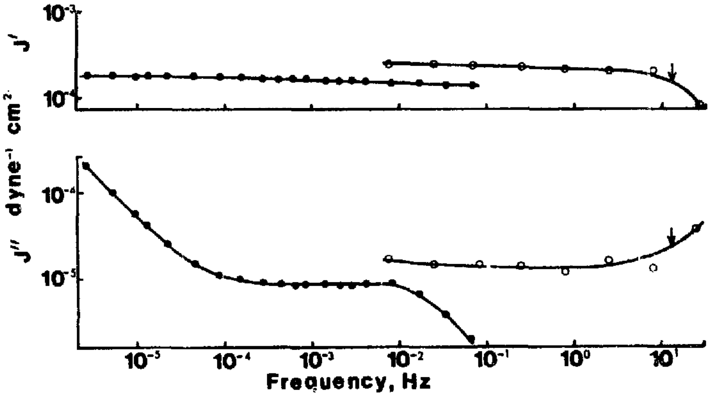


Fig. 9. Variation of J'(ω) and J''(ω) with frequency for 3% neutralized Carbopol 940 gels. Solid symbols indicate transformed creep data and open symbols indicate experimental data. The arrows indicate resonant frequency, 13.2 Hz.

sometimes scattered, tended to indicate increased consistency with increased temperature at low frequencies and the reverse trend at higher frequencies. Fig. 8 shows time-temperature equivalence plots for storage and loss compliances (J' and J'') derived from these data.

Transformed data for neutralized 3% Carbopol 940 and 941 gels are in Figs. 9 and 10. On each plot the resonant frequency of the rheogonimeter (13.2 Hz, which is associated with anomalous behaviour) is indicated by an arrow. Plots consist of the appropriate function derived by direct oscillatory measurements over a frequency range of 7.91 X 10^{-3} to 25 Hz and the same function derived from transformed creep data over a frequency range of 2.65 X 10^{-6} to 6.80 X 10^{-2} Hz.

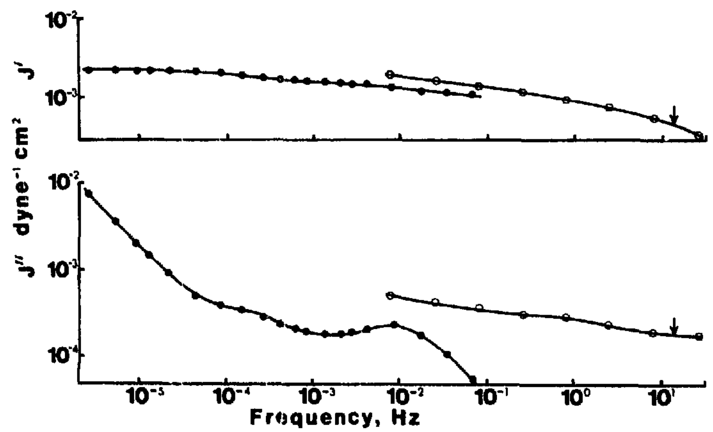


Fig. 10. Variation of J'(ω) and J''(ω) with frequency for 3% neutralized Carbopol 941 gels. Solid symbols indicate transformed creep data and open symbols indicate experimental data. The arrows indicate resonant frequency, 13.2 Hz.

DISCUSSION

The accuracy of the equations used to derive G′ and η' depends mainly on the error associated with the measurement of the input and output amplitudes and the phase lag. The manufacturers of the digital transfer function analyzer quote an accuracy of 0.1% full scale deflection for amplitude measurements and ±10 minutes of arc for resolution of angles. Although the former is unlikely to have a significant effect on derived data, under certain circumstances, the latter could lead to serious errors. Thus, for a phase lag of 1° the possible error in η' is ±15%; with a 2° phase lag the error would be ±7% and with a 5° phase lag error falls to ±3%. The error associated with the calculation of G′ is less significant, e.g. for 1° and 2° phase lags the error is approximately ±2% and for a 5° lag the error is approximately 1%. These errors are quoted for an amplitude ratio of 0.9; the effect of varying the amplitude ratio was also investigated and was found to have a relatively small effect on the calculation of these errors. These data indicate that calculation of G′ is unlikely to cause serious errors but calculation of η' using small phase lags can lead to significant error in both this and any other parameter derived from η' i.e. G″ and tan ϕ.

The generalized Maxwell model provides a convenient way for visualizing how viscoelastic materials behave when oscillated (Barry, 1974). At high frequencies the springs can elongate and contract under the imposed oscillatory shear, but the dashpots have little time to move. Energy is stored in each cycle of deformation and the material behaves as an elastic solid. At low frequencies the springs can elongate and the dashpots also have time to move to extensions which greatly exceed those of the springs. Energy is dissipated and the sample behaves as a liquid. At intermediate frequencies both springs and dashpots provide contribution and viscoelastic behaviour is observed. The frequency response may be related to the retardation time, τ (Barry, 1974). Thus, if $1/\omega \gg \tau$, viscous flow predominates; if $1/\omega \ll \tau$, elastic deformation occurs and when $1/\omega$ lies between these two extremes, the system exhibits viscoelastic behaviour. The largest experimental value of $1/\omega$ was 20, which was similar to the values of τ_3 obtained previously (Barry and Meyer, 1979). Thus, using the condition given above elastic behaviour should predominate and this was confirmed by the derived data.

From Figs. 1–4 it can be seen that in general, as the frequency increased G′ gradually increased and η' decreased more or less monotonically through several decades. This behaviour conforms with the mechanical model described above. The relationship between G″ and η' or G′ and η'' can be inferred from Eqns. 1 and 2. Thus, in regions where G″ or G′ are approximately parallel to the frequency axis, η' and η'' will be inversely proportional to the frequency. This behaviour is clearly shown in Figs. 1–4.

Discontinuities occurred in many of the curves at frequencies close to the natural frequency of the rheogoniometer (13.2 Hz). In this frequency region the theory of forced oscillation predicts that all viscous and elastic liquids will exhibit amplitude ratios and phase angles of unity and zero respectively. At frequencies above resonance phase angles become phase leads. Amplitude ratios for viscous liquids are usually less than one and elastic liquids often exhibit prominent peaks. Amplitude ratios for Carbopol gels were generally greater than one in this region. The natural frequency region is most sensitive to change in material parameters. However, to investigate this region requires detailed measurements at frequencies close to resonance which are not possible with the rheogoniometer. Thus, data in this region are indicated by dotted lines in Figs. 1–4. Previous authors have also noted irregularities in data obtained at frequencies close to resonance, e.g. Warburton and Davis (1969), Barry and Eccleston (1973a, b) and Jones and Walters (1971). The last authors suggested that these irregularities were due to small experimental errors which were magnified at frequencies close to resonance.

G′ and G″ change little over the frequency range which indicates that the material is being examined in the plateau region of viscoelasticity (Ferry, 1970). This region was observed in other pharmaceutical semisolids such as creams and ointments (Davis, 1971a; Barry and Eccleston, 1973a, b) and in biological fluids such as mucin and sputum (Davis, 1971b; Lutz et al., 1973; Davis and Dippy, 1969). However, the plateau region for the pharmaceutical systems did not extend over as broad a frequency range as that observed for the Carbopol gels. For polymeric systems the size of this region is related to the molecular weight of the polymer. The plateau region is exhibited by both cross-linked and high molecular weight uncross-linked polymers. Long range configurational rearrangements for the former are suppressed by cross-links and for the latter by entanglements. Thus similar moduli are observed regardless of frequency. For uncross-linked polymers at sufficiently low frequencies, time is available for these entanglements to slip and flow past each other and G′ will approach zero. For truly cross-linked polymers the plateau region will extend to the lowest frequencies. As the frequency scale extends only over a relatively short range it is difficult to decide at this stage whether the Carbopols are cross-linked or not.

As previously indicated by the creep data (Barry and Meyer, 1979) the moduli and viscosities obtained for Carbopol 940 gels were generally higher than those for Carbopol 941 gels. The exceptions were G′, and η' for the 5% and 10% gels where the data for both types of gels were similar. Although this behaviour was not observed in the creep experiments it was shown in the continuous shear results obtained with the low shear rate regime. This indicates a correlation between the shearing conditions in oscillatory tests and continuous shear tests. A similar correlation was previously suggested for other pharmaceutical creams and ointments and for biological systems such as sputum (Warburton and Davis, 1969; Davis and Dippy, 1969). In all samples examined G′ was greater than G″, i.e. the elastic contribution is greater than the viscous contribution. This agrees with the dominant elastic behaviour of Carbopol gels observed in creep. At high frequencies G′ should approach G_0, the instantaneous elastic modulus derived in creep. Values of G_0 and G′ (obtained at 7.91 Hz) for neutralized Carbopol 940 gels differed by 30–40% and for neutralized Carbopol 941 gels the difference was 20–40%. For the unneutralized systems the difference was less; 21% and 29% for 3% and 5% Carbopol 940 gels and 17% and 6% for 3% and 5% Carbopol 941 gels. In view of the practical difficulties in deriving G_0 (i.e. difficulty of applying an instantaneous stress and recording an instantaneous strain), these differences are not surprising and in fact are quite acceptable.

Comparison of data for the neutralized and unneutralized gels shows that, except for Carbopol 940 gels close to resonance, both systems behave similarly in oscillation. This behaviour agrees with that observed in creep where the unneutralized systems exhibited similar consistencies to those obtained for the neutralized systems. Also G′ and G″, for the unneutralized gels, show a smaller variation with frequency than that observed for the neutralized gels. This suggests the presence of a more rigid structure in the unneutralized systems and confirms the creep results where these systems were characterized by a shorter viscoelastic region.

Another parameter associated with G′ and G″ is the loss tangent, which is the tangent of the phase angle. Tan ϕ conveys no physical magnitude but is a measure of energy lost to energy stored in a cyclic deformation ($\tan\phi = G''/G'$), and this provides a comparative parameter that combines both the elastic and viscous contributions. Davis (1971a) suggested that a plot of log tan ϕ versus log frequency could be used as a consistency spectrum for comparison of materials and for following rheological changes, e.g. storage stability and quality control. However, as G′ and G″ changed slowly with frequency, tan ϕ also showed little change with frequency (Fig. 5) and, thus, interpretation of the plots can only be of a general nature. For both Carbopol 940 and 941 gels, values of tan ϕ are less than 1 which indicates the predominant elastic nature of the gels. Further confirmation of the trends indicated by the creep experiments is shown by the relative values of tan ϕ for the neutralized and unneutralized systems.

As shown in Figs. 2 and 4, η' at low frequencies was high for all experimental systems (10^3–10^4 poise). At very low frequencies, viscoelastic theory predicts that η' should approach η_0, the residual viscosity derived in creep. The lowest frequency used in this work was 7.91×10^{-3} Hz which is equivalent to a creep time of approximately 20 s. After this time, retarded elastic mechanisms still influenced the creep behaviour of Carbopol gels. This explain why η' for each gel, derived at 7.91×10^{-3} Hz, was approximately half the value of the corresponding residual viscosity obtained in creep. It would be necessary to use much lower frequencies in order to obtain values of η' that were close to the residual viscosities and work at such low frequencies would involve experimental difficulties. The digital transfer function analyzer required one cycle to lock onto the input sine wave and then an additional cycle to compare input and output sine waves. The long experimental times required for this process at low frequencies would increase evaporation errors, especially for parallel plate geometry. This practical point illustrates the importance of supplementing one type of viscoelastic test with another in order to derive data over a broad time scale. Thus, as previously suggested by Davis (1971a) there are three different frequency regions for testing pharmaceutical semisolids; (a) $\omega > 10^{-1}$, oscillatory testing only; (b) $4 \times 10^{-3} < \omega < 10^{-1}$, creep and oscillatory methods; (c) $\omega < 4 \times 10^{-3}$, creep testing only.

Increase in polymer concentration increased both the elastic and viscous moduli for Carbopol gels and these trends were similar at several frequencies (Figs. 6 and 7). The plots of η' versus concentration for Carbopol 940 gels exhibited irregularities and values of G″ for the same material were scattered; to avoid confusion in Fig. 6 the latter data were not connected. As discussed above, these parameters are subject to large errors and no particular significance is attached to these irregularities. As previously indicated, in creep and continuous shear the relationship between a particular rheological parameter and polymer concentration was logarithmic. However, this relationship for the oscillatory data does not appear to be a simple one (i.e. log oscillatory parameter $\neq K'C + B'$, where K' and B' are constants and C is the polymer concentration). Another similarity between creep and oscillatory data obtained at different polymer concentrations is that for Carbopol 941 gels data tend to increase rapidly with initial increase in polymer concentration and then to flatten out, whereas for Carbopol 940 gels the data tend to increase at a more or less constant rate. This suggests that for Carbopol 941 gels a major part of the gel structure is formed at low concentrations. For Carbopol 940 and Carbopol 941 above 3–4% polymer concentration the dominant structures are already present and increase in polymer concentration provides a less significant increase in consistency.

When Carbopol gels were examined at different temperatures no distinct trends were observed. This may have been due to evaporation effects or to the temperature differences being too small to affect the rheological properties of the gels in oscillation. However, when these data were combined by the method of reduced variables satisfactory composite plots were obtained over a slightly increased frequency range showing that this method is applicable to the Carbopol systems (Fig. 8). This type of agreement is usually obtained for amorphous or slightly cross-linked polymers (Karas and Warburton, 1961). A similar transformation was performed for data obtained for samples of petrolatum but, due to temperature-induced phase transitions, composite curves were not obtained (Grace, 1971). The values of J''_p for Carbopol 940 gels were scattered because of the error associated with calculating this parameter for materials exhibiting small phase lags. In general, the compliances gradually increased with decreased frequency. The relatively small changes in values of J'_p and J''_p indicates that the plateau region extends over a broader frequency range than initially shown by the plots of G′ and G″ versus frequency in Figs. 1 and 3. Also J'_p is greater than J''_p for each type of gel which again emphasizes the elastic nature of the gels. Comparison of the curves in Fig. 8 with published data suggests that Carbopol gels consist of either a high molecular weight amorphous polymer with long side chains or a lightly cross-linked amorphous polymer or a highly crystalline polymer (Ferry, 1970). The extensive plateau region suggests that from these possibilities the high molecular weight cross-linked amorphous polymer seems the more likely, although the latter is not entirely consistent with the presence of a residual viscosity as observed in creep. However, the behaviour of Carbopol gels over the extended frequency range shown in Figs. 9 and 10 strongly resembled that of a high molecular weight amorphous polymer with long side chains rather than a lightly cross-linked polymer (Ferry, 1970). This conclusion is consistent with the creep results and illustrates how a knowledge of material behaviour over a broad time or frequency scale is useful in interpreting results. Thus, the dominant elastic behaviour of Carbopol gels may be explained in terms of side chain entanglements, with the possibility of hydrogen bonding. The permanent viscous flow is due to inter-chain movements.

In general, at the overlapping frequencies, the transformed values of $J''(\omega)$ for both types of gels were approximately 50% lower than the experimentally obtained data. The transformed values of $J'(\omega)$ for Carbopol 940 gels were approximately 40% lower and for Carbopol 941 gels approximately 20% lower than the experimental data. These results imply that the gels were higher in consistency during transient tests than during oscillatory excitation. Several factors may account for this behaviour. The loading procedure for the two tests differs considerably. In the creep tests, the samples were loaded and allowed to stand overnight at the investigation temperature before being tested so that the stresses induced by the loading procedure could relax. In the oscillatory test, the sample was placed on the lower plate and deformed into a thin film as the upper plate was lowered to obtain the required gap width. The test procedure was performed immediately after loading and no time was allowed for structure to reform. Thus, the consistency of a sample during oscillation would be less than the consistency of a similar sample during transient testing. The method of calculating the viscoelastic parameters from creep tests does not take into account the 'end effect'. Neglect of this effect increases the mean shear stress calculated. Thus, if the 'end effect' were allowed for, the transient parameters would move closer to the relevant oscillatory data. The calculation of $J'(\omega)$ and $J''(\omega)$ at high frequencies requires a knowledge of J(t) (the total shear compliance at time = t) at times shortly after the onset of stress. As previously discussed (Barry and Meyer, 1979) the initial part of the creep curve is subject to error due to the inertia of the viscometer, etc., and, thus, in this region transformed data may be scattered and tend to deviate from the experimental points. This is indicated by the plots of $J''(\omega)$ versus frequency (Figs. 9 and 10) which show increasing deviation from experimental data above approximately 10^{-2} Hz. Similar deviations are not shown by the plots of $J'(\omega)$ versus frequency as elastic behaviour is relatively constant with respect to time. A further source of error that will affect values of $J''(\omega)$ at low frequencies is the accuracy with which η_0 can be determined. Errors in the oscillatory measurements may be caused by evaporation from the parallel plates during the comparatively long experimental times required for tests at low frequencies and by the accuracy of phase lag measurements if the phase lags are small. This last source of error will predominantly affect values of $J''(\omega)$. However, discrepancies in the oscillatory parameters are not obvious and smooth trends are exhibited by the data.

In view of the many possible sources of error outlined above, the agreement shown between transformed and experimental data is reasonable. Previous authors obtained similar agreement for data obtained for pharmaceutical creams and these authors considered this to be quite acceptable (Eccleston et al., 1973). Thus, although the accuracy of the conversion technique was limited at overlapping frequencies it was assumed that transformed data derived at long frequencies were representative of the values that would be obtained if it were possible to conduct oscillatory experiments in this frequency range.

The plots of $J'(\omega)$ are characterized by an almost constant response over the entire frequency range. This behaviour is typical of cross-linked or highly entangled polymers. According to linear viscoelastic theory $J'(\omega)$, at very low frequencies, should approach the total recoverable elastic compliance in creep (i.e. $J(t) - t/\eta_0$). Experimental data obtained in previous work (Barry and Meyer, 1979) at t = 120 min was compared with transformed data obtained at the equivalent frequency. The data were within 2% at all concentrations, showing good agreement with the theoretical prediction.

Plots of $J''(\omega)$ show an increase at approximately 10^{-4} Hz. This change in behaviour indicates that below this frequency, the materials are no longer examined in their plateau region and that the contributions of the dissipative elements are becoming more prominent. At low frequencies $J''(\omega)$ increases rapidly and exceeds $J'(\omega)$ at $2-4 \times 10^{-6}$ Hz for Carbopol 940 gels and at $8-10 \times 10^{-6}$ Hz for Carbopol 941 gels. These different frequencies indicate that eleastic properties are more dominant in Carbopol 940 gels than in Carbopol 941 gels. Below these frequencies viscous properties predominate and $J''(\omega) = 1/\omega\eta$ from which it can be inferred that a double log plot of $J''(\omega)$ versus frequency will have a slope of −1. Good agreement with this relationship was shown by the transformed data.

In general, the oscillatory data indicated that Carbopol gels were highly elastic systems. Many of the trends exhibited by the oscillatory data confirmed results previously obtained in creep and some correlation with continuous shear results was observed. However, it was difficult to interpret the results on a molecular level because of the relatively small changes observed in the viscoelastic parameters over the experimental frequency range. It may be possible to derive more information by using either higher temperatures or lower frequencies or a larger sample gap width. But these techniques are associated with practical problems because results obtained at higher temperatures or lower frequencies would suffer from evaporation effects and for the purposes of analysis of the experimental data the gap width should be kept small.

A more feasible alternative method of extending the frequency range is the transformation of transient results. The trends exhibited by the functions plotted in Figs. 9 and 10 are in good agreement with the theoretical predictions and conform with the generalized Maxwell model analogy used to represent the behaviour of the gels in oscillation. This agreement suggests that in both types of test the systems were examined essentially in their rheological ground state and that the assumption that transformed data may be used to predict rheological behaviour at low frequencies, normally inaccessible to the rheogoniometer, is valid. However, in view of the limitations of the transformation process at high frequencies it is not possible to obtain accurate dynamic data in this region without the use of the rheogoniometer.

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