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Research Papers

THE RHEOLOGICAL PROPERTIES OF CARBOPOL GELS I. CONTINUOUS SHEAR AND CREEP 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

The effect of physical and chemical variables on consistency of Carbopol 940 and 941 gels was investigated by continuous shear rheometry. Gels provided plastic flow curves with negligible hysteresis. Continuous shear properties were not greatly affected by centrifuging, milling, temperature cycling, and ageing. Initial addition of neutralizing agent (0–6% w/w for 3% gels) markedly increased consistency; further addition caused a more gradual increase. Daylight reduced consistency. Apparent viscosities varied exponentially with concentration. Increased temperature gradually decreased apparent viscosity. Solvents had a variable effect on apparent viscosities which could not be correlated with solvent viscosity nor molecular weight. Apparent viscosities for gels neutralized with different bases were independent of type of base used.

Small strain testing investigated fundamental properties of Carbopol gels and determined the effect of polymer concentration, temperature, neutralization, different solvents and neutralizers. Gels were linear viscoelastic and to a first approximation were elastic solids. Creep compliance varied exponentially with concentration and showed no correlation with solvent or neutralizer type.

INTRODUCTION

The Carbopols (B.F. Goodrich Co.) were introduced in the mid- to late-1950s as a group of hydrophilic, colloidal gums with improved thickening properties compared with natural gums. The synthetic nature of these polymers, which allows close quality control and marked thickening and suspending properties at relatively low concentrations, has led to their wide usage in the pharmaceutical and cosmetic industries. However, the rheological investigations accompanying their increased use have utilized mainly empirical techniques (Fischer et al., 1961; Van Oudtshoorn and Potgieter, 1971) and thus little is known of the fundamental rheological properties of their systems.

Carbopols were originally defined as extremely high molecular weight carboxyvinyl polymers containing many carboxyl groups (Dittmar, 1957). More recently they were described as polyacrylic acid polymers cross-linked with allyl sucrose (Martin, 1965; Saito and Taniguchi, 1973). Infra-red spectroscopy has shown that the polymer consists mainly of methyl and methylene groups (Fischer et al., 1961). Substituent groups are arranged syndiotacticly along the polymer chain and this stereoregularity is not affected by neutralization (Bardet et al., 1975a). Molecular weights were variously quoted as: Carbopol 934, $(22 \pm 3) \times 10^6$; Carbopol 940, $(29 \pm 4) \times 10^6$; Carbopol 941 $(21 \pm 3) \times 10^6$ (Testa, 1970), Carbopol 940, $(2.4 \pm 0.24) \times 10^6$ (Bardet et al., 1975b), Carbopol 934, 3×10^6 (Bloemers and Van der Horst, 1975; Kumar, 1976). This variation in molecular weight was explained by other investigations which showed that Carbopol 941 contains up to 20% soluble uncross-linked polyacrylate and that the molecular weight of Carbopol 940 is log normally distributed (Taylor and Bagley, 1974, 1975; Bardet et al., 1975c). Thus Carbopols may be assumed to be highly polydisperse.

When Carbopols disperse in water, cloudy, acidic dispersions of low consistency form. Neutralization increases consistency and reduces turbidity. Strong bases such as sodium hydroxide should be added as 10% solutions to prevent polymer degradation, but amines (e.g. triethanolamine) and weak inorganic bases (e.g. ammonium hydroxide) can be used in concentrated form.

Several mechanisms were suggested to account for the formation of Carbopol gels. In acid conditions a small proportion of the carboxyl groups present on the polymer chain dissociate, producing a flexible coil structure. Base causes further dissociation resulting in electrostatic repulsion between the charges on the polymer. Thus a gel forms as the molecules extend and become rigid. Further base thins the gel because the cations screen the carboxyl groups and so the electrostatic repulsion decreases (Dittmar, 1957). The consistency does not decrease when excess amine is added to a Carbopol dispersion, possibly because steric effects prevent screening of the charged carboxyls. Another mechanism proposed to account for the thickening of hydrophilic, organic solvents, without neutralization, involves hydrogen bonding of the solvent molecules to the carboxyl groups on the polymer. Orientation of the solvent molecules along the polymer chain produces a rigid structure (Lang, 1972). Hydrogen bonding in aqueous conditions must also occur but because the water molecules are small this has only a minor effect on the flexible nature of the polymer. A mechanism that takes the cross-linked nature of the polymer into account involves the absorption of water by the polymer to form a gel consisting of macroscopic, swollen particles (Taylor and Bagley, 1974, 1975; Bagley and Taylor, 1974). The close packed arrangement of the particles can be deformed and in extreme conditions the particles may be broken down causing a permanent loss in gel strength. There is no definite evidence for any one mechanism and it seems likely that gelation occurs by a combination of the above processes.

In the present work some of the rheological properties which are particularly relevant to pharmaceutical and cosmetic formulation were investigated. A brief survey of the effect of mixing, light, time, temperature cycling and amount of neutralizing agent on the continuous shear properties of Carbopol gels is given. In addition small strain and continuous shear techniques were used to investigate the effect of polymer concentration, temperature and different solvents and neutralizing agents on the general rheological nature of the gels and characterize their fundamental viscoelastic behaviour.

MATERIALS AND METHODS

Carbopol 940 and 941 were selected. Carbopol 934 was omitted because it is similar to Carbopol 940 and was used in several previous investigations. The main differences are that Carbopol 940 forms clear gels of slightly higher consistency and over a broader pH range than Carbopol 934.

Samples of Carbopol 940 and Carbopol 941 were obtained from Honeywill Stein Ltd., London and stored over phosphorous pentoxide. Polymer equivalent weights were obtained by potentiometric titration of a 0.1% Carbopol solution with 0.098 N sodium hydroxide. Mean of five titrations gave 75.9 ± 0.4 and 74.5 ± 0.2 for Carbopol 940 and 941, respectively. These values confirmed the approximate value of 75 given by the manufacturer. Thus, the latter was considered sufficiently accurate for the preparation of bulk samples of neutral gels.

Triethanolamine [1] B.P.C., was selected as the main neutralizing agent because as an inorganic base it would have no undesirable effects on the Carbopols. Monoethanolamine [1] B.P.C., diethanolamine [1] (98% pure) and sodium hydroxide [1] (Analar grade) were also used.

Water, freshly distilled from an all glass still, ethylene glycol [1], propylene glycol [2] B.P., and glycerin [2] B.P. were used as solvents.

Preparation of gels

In general gels were prepared in 500 g quantities so that several rheological tests could be performed on the same batch. The required weight of solvent was agitated at approximately 300 r.p.m. with a stirrer consisting of two paddle impellers (diameter 4.5 cm, separation of impellers 6 cm) on a common shaft. The Carbopol was added into the vortex; when all was dispersed, stirring was stopped and the liquid was allowed to stand so that entrained air could escape. If any lumps of partially wetted Carbopol were present at this stage the dispersion was discarded and a new batch was prepared. Gels containing more than 6% Carbopol were stored overnight to ensure maximum dissolution of the polymer. The dispersion was then stirred at the maximum speed that did not produce a vortex and the calculated weight of base (determined using an equivalent weight for Carbopol of 75) was added. Mixing was continued until a clear homogeneous gel was obtained. For gels containing 5% polymer or more the mixer was not powerful enough to disperse the neutralizing agent so it was mixed in with a spatula. Both mixing processes invariably entrapped air in the gel. This was removed by centrifuging the gel for 10–20 min at 3000 r.p.m. To determine if this method of deaeration influenced the continuous shear properties of Carbopol gels they were tested as follows (for full rheological details, see below).

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

[2] J.M. Loveridge, Southampton.

Rheograms for 1% and 3% neutralized and unneutralized gels were obtained before and after centrifugation at 3000 r.p.m. for 15 min and after a second period of centrifugation. Agreement between the curves was within ±2%, i.e. the accuracy of the viscometer. This technique was therefore considered suitable for the preparation of gels for all subsequent tests. After centrifugation the gels were transferred to 120 ml glass jars which were stored in the dark at 25 ± 1°C.

To investigate the effect of a typical pharmaceutical working procedure, 1% and 3% neutralized and unneutralized gels were worked in a standard manner using a triple roller mill (Erweka-apparatebau Gmb, G.F.R.). During the passage of the sample through the mill it was twice subjected momentarily to high shear rates as it passed between the rollers. The maximum shear rates in each gap were approximately 6300 s^{-1} and 10,300 s^{-1}, calculated by dividing the linear velocity differences at the roller surfaces by the gap distances between them, assuming plane laminar flow in the gap. Rheograms of the gels were obtained before and after a single passage through the mill.

To determine the effect of neutralizer concentration on the continuous shear properties of Carbopol gels, 6% polymer dispersions were divided into 21 lots. Different amounts of triethanolamine (0–40%) were added to the samples which were then adjusted to 3% gels with water. The apparent pH and flow curves were obtained after three days storage.

The effect of storage time and light on 3% gels was examined by storing samples in the dark and in daylight on the bench and testing them immediately after preparation and at intervals during six weeks. As a further assessment of the physical stability of Carbopols, 3% gels were tested initially after two days storage at 25 ± 1°C and after each of three cycles of three days at 3°C and three days at 40°C.

In order to fully characterize the rheological behaviour of Carbopol gels a 1–10% range of neutralized gels was examined three days after preparation using both continuous shear and creep tests. For comparison 1, 2, 3 and 5% unneutralized gels were also tested. The behaviour of 1% and 3% gels with respect to temperature was similarly examined.

As the final part of this work neutralized and unneutralized 3% gels were prepared using either different solvents with triethanolamine as the neutralizing agent or using water as the solvent with different neutralizers. These gels were examined after three days storage using both rheological techniques.

Instrumental rheology

Continuous shear experiments were performed using a Ferranti–Shirley cone and plate viscometer with automatic flow curve recorder unit, automatic cone-plate setting device and X–Y plotter (Van Wazer et al., 1963; Mckennell, 1954, 1956; Barry, 1974). Samples were measured onto the plate from a 2 ml plastic syringe, the end of which was removed so that it did not taper and thus did not significantly shear the gel. The viscometer with medium cone was employed in automatic mode to obtain rheograms at 25 ± 0.1°C using two shear rate regimes: (a) 0.0 to 1754.0 to 0.0 s^{-1} in 1200 s and (b) 0.0 to 175.4 to 0.0 s^{-1} in 1200 s. These regimes were modified for certain tests. For the general rheological tests (i.e. investigation of the effect of mixing, neutralizer concentration, time, light and temperature cycling) a 24-s sweep time was used. although short sweep times are less accurate and can cause instrumental artefacts (Cheng, 1968; Barry, 1974) the many samples tested required a short time. The short sweep time was also used for the investigation of temperature effects to minimize evaporation. No shear artefacts were observed.

The 1% unneutralized gels had relatively low consistencies and could not be accurately tested with the medium cone. Thus tests were performed with the large cone which gave preset maximum shear rates of 1709 s^{-1} and 170.9 s^{-1}. In some cases the consistency of the gels was very high and it was necessary to use the small cone. This gave preset maximum shear rates of 1638 s^{-1} and 163.8 s^{-1} and its use will be indicated where appropriate.

Creep viscometry was performed using a concentric cylinder reaction air turbine viscometer, in which an air bearing centered and supported the inner cylinder and turbine air applied a constant torque (Barry and Grace, 1970; Barry, 1974). Approximate linearities were determined by applying stresses from 2–170 dyne cm^{-2} and measuring the resultant strain. Provided the ratio of strain to stress was constant the material was assumed to respond in a linear viscoelastic manner. After samples had relaxed fully creep tests were performed by applying a stress for 90 min, by which time the strain response was essentially linear with time. Recovery curves were obtained and compared with the theoretical recovery. Provided agreement was within ±2% it was assumed that the test was conducted in the linear viscoelastic region. The creep curves (compliance versus time) were analyzed graphically in terms of discrete viscoelastic models (Warburton and Barry, 1968; Barry, 1974).

RESULTS

Apart from the temperature studies all results were obtained at 25 ± 0.1°C and apparent viscosities were derived from the apices of the flow curves and are quoted as means of duplicate determinations. Rheograms for 1% and 3% neutralized and unneutralized Carbopol 940 gels and 1% and 3% neutralized Carbopol 941 gels showed plastic flow behaviour with negligible hysteresis for both the high and low shear rate regimes. Rheograms ior 1% and 3% unneutralized Carbopol 941 gels were similar in shape but gave anticlockwise hysteresis loops, particularly with the 3% gel and the high shear rate regime. For the 1% and 3% neutralized gels a single passage through the triple roller mill reduced the apparent viscosities of Carbapol 940 gels by less than 3% and Carbopol 941 gels by less than 6%. Initial apparent viscosities, obtained with the high shear rate regime, for 1% and 3% Carbopol 940 gels were 6.61 and 13.7 poise respectively and for Carbopol 941 gels 3.42 and 9.38 poise respectively. For the unneutralized systems milling reduced the apparent viscosity of Carbopol 940 gels by up to 5% (initial apparent viscosities were 0.502 and 2.99 poise for the 1% and 3% gels, respectively) and the Carbapol 941 gels by up to 7.4% (initial apparent viscosities were 0.855 and 2.82 poise for the 1% and 3% gels, respectively). The unneutralized systems, particularly the Carbopol 941 gels, demonstrated a slight reduction in hysteresis loop area. In both cases, the data from the low shear rate regime indicated similar trends.

The apparent viscosities and pH values for both types of gels increased rapidly with initial addition of triethanolamine (0–6% w/w). Further addition produced little pH change and a more gradual increase in apparent viscosity. At high concentrations of triethanolamine (30–40% w/w) the apparent viscosities again increased rapidly (Fig. 1a, b).

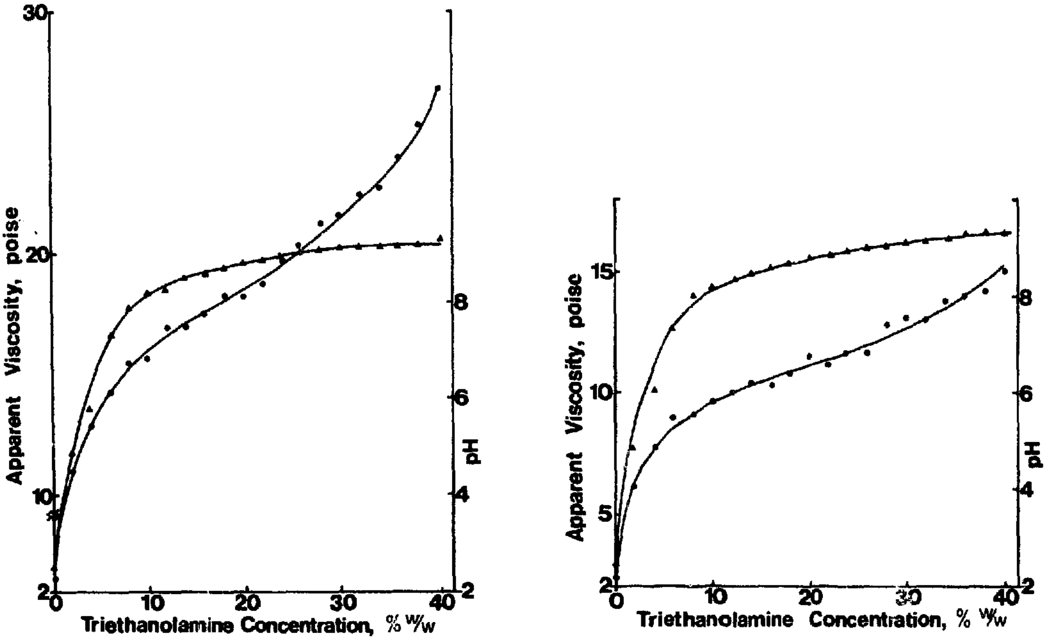

Fig. 1. a: apparent viscosities (●), derived with the light shear rate regime, and pH values (▲) for Carbopol 940 gels containing different amounts of triethanolamine. b: apparent viscosities (●), derived with the high shear rate regime, and pH values (▲) for Carbopol 941 gels containing different amounts of triethanolamine.

For samples stored in the dark for 6 weeks the apparent viscosities of the Carbopol 940 gels increased by 1.4% and 2.1% for the neutralized and unneutralized systems respectively; the apparent viscosities of Carbopol 941 gels decreased by 2.6% and 4.5% for the neutralized and unneutralized systems respectively. The consistencies of gels exposed to daylight for 6 weeks reduced markedly. The apparent viscosities of the neutralized systems decreased by 12% for Carbopol 940 and 24% for Carbopol 941. For the unneutralized systems the apparent viscosities were reduced by 35% and 62% for Carbopol 940 and 941 respectively (Table 1). The unneutralized Carbopol 941 system also demonstrated a marked reduction in hysteresis loop area.

Temperature cycling caused an insignificant (less than 2%) increase in the apparent viscosities of the neutralized systems; unneutralized systems increased by 4%.

When the 1–10% range of gels were examined, neutralized Carbopol 940 systems provided plastic flow curves with no spur points and negligible hysteresis (Fig. 2).

Neutralized Carbopol 941 gels gave similar flow curves and as the polymer concentration increased spur points developed (Fig. 3). The apparent viscosities derived for both systems are in Table 2.

Flow curves for the unneutralized Carbopol 940 gels were similar to those of the neutralized systems but showed a marked decrease in consistency compared with the latter group. Unneutralized Carbopol 941 gels gave plastic flow curves with hysteresis loops which increased in area with increase in polymer concentration. Apparent viscosi-

TABLE 1

APPARENT VISCOSITIES FOR NEUTRALIZED AND UNNEUTRALIZED CARBOPOL 940 AND 941 GELS WHICH WERE STORED IN THE DARK AND IN DAYLIGHT AND TESTED OVER 6 WEEKS

Data in parenthesis are for samples stored in daylight.

Time of test, days	Apparent viscosity, poise			
	Carbopol 940		Carbopol 941	
	Neutralized	Unneutralized	Neutralized	Unneutralized
Initial	14.2 (14.5)	2.78 (2.74)	9.01 (8.94)	2.65 (2.69)
2	14.2 (14.3)	2.73 (2.58)	8.83 (8.79)	2.59 (2.58)
4	14.2 (14.4)	2.71 (2.55)	8.92 (8.74)	2.61 (2.49)
8	14.3 (14.3)	2.71 (2.53)	8.87 (8.53)	2.61 (2.37)
12	14.4 (14.2)	2.75 (2.48)	8.81 (8.32)	2.59 (2.22)
21	14.4 (14.0)	2.78 (2.39)	8.88 (7.73)	2.57 (1.96)
42	14.4 (12.7)	2.84 (1.77)	8.78 (6.81)	2.53 (1.03)

ties were markedly lower than those obtained for the neutralized systems (Table 2, Fig. 4).

For the neutralized systems examined at 10 temperatures over the range of 5–70°C, increased temperature gradually decreased the apparent viscosity and removed any hysteresis. The apparent viscosity data were used in Arrhenius-type plots and the values

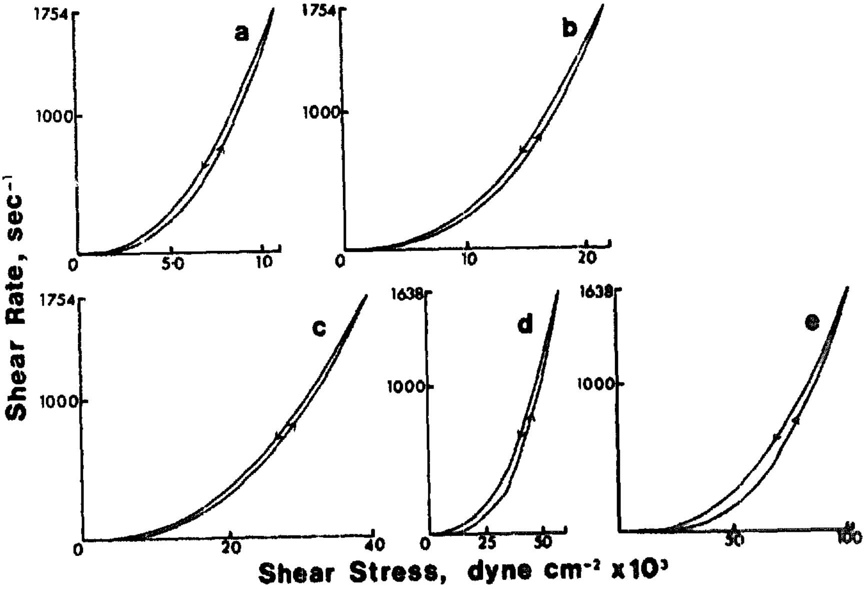

Fig. 2. Flow curves for neutralized gels containing different amounts of Carbopol obtained using the high shear rate regime. a: 1%; b: 3%; c: 5%; d : 7%, e: 10%.

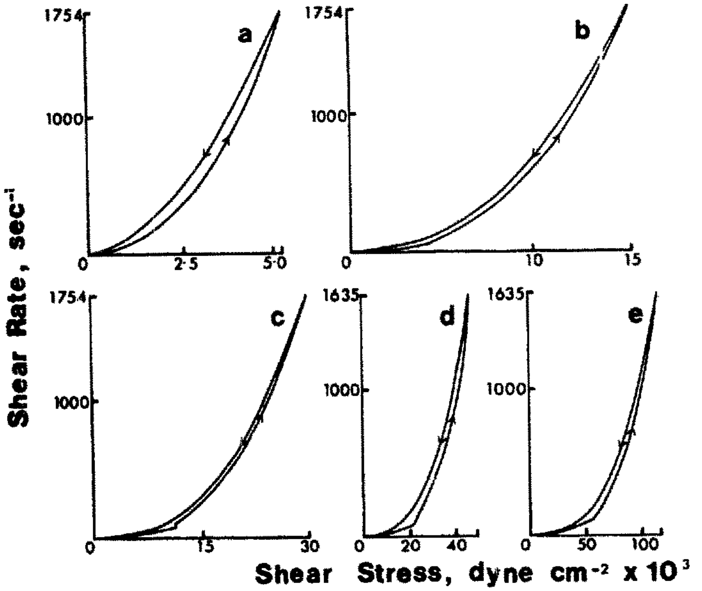

Fig. 3. Flow curves for neutralized gels containing different amounts of Carbopol 941 obtained using the high shear rate regime. a: 1%; b: 3%; c: 5%; d: 7%; e: 10%.

of apparent activation energy for viscous flow derived from these plots are given in Table 3.

For unneutralized Carbopol 940 gels examined at 8 temperatures over the range 10–60°C, increased temperature reduced hysteresis loop area and increased apparent viscosities. As an increase in apparent viscosity is inconsistent with an activation energy for viscous flow these data were not used to derive such values. Flow curves for unneutralized Carbopol 941 gels showed a marked increase in hysteresis loop area as the test temperatures approached 10°C; however, the apparent viscosities obtained from these curves did not show a consistent trend over the range 10–25°C. Above 25°C the apparent viscosities gradually decreased with increase in temperature and thus only the data obtained at 25°C and above were used to derive values of apparent activation energy for viscous flow (Table 3). The restricted temperature range used for these systems was necessary because of their anomalous behaviour at low temperatures and their greater susceptibility to evaporation effects at high temperatures.

Gels prepared with non aqueous solvents gave plastic flow curves which demonstrated increased consistency and hysteresis compared with the corresponding pure aqueous systems. The apparent viscosities for gels neutralized with different bases were not related to the type of neutralizer but rather to the final pH of the system. Apparent viscosities and pH for these systems obtained with the high shear rate regime are given in Table 4; the data obtained with the low shear rate regime showed similar trends.

In creep the approximate linearity checks indicated that the gels were linear viscoelastic over the range tested. Fig. 5 shows the effect of increased polymer concentration on the creep behaviour of Carbopol gels. Graphical analyses provided an 8-element mechanical model (a Maxwell unit in series with three Voigt units). In theory there may be an

TABLE 2

APPARENT VISCOSITIES AND pH VALUES FOR NEUTRALIZED AND UNNEUTRALIZED GELS CONTAINING DIFFERENT CONCENTRATIONS OF CARBOPOL 940 AND 941

Figures in parentheses are for the corresponding unneutralized gels.

Carbopol 940 concentration, %	Apparent viscosity, poise		pH
	High shear rate regime	Low shear rate regime	
1	6.19 (0.331)	23.9 (1.04)	7.50 (2.95)
2	9.13 (1.15)	35.1 (4.12)	7.46 (2.70)
3	12.4 (2.27)	49.9 (9.10)	7.40 (2.55)
4	16.9	65.1	7.40
5	22.3 (5.35)	84.8 (24.9)	7.40 (2.45)
6	28.3 [a]	108	7.30
7	35.8 [a]	148	7.43
8	43.8 [a]	176	7.30
9	51.9 [a]	213	7.30
10	62.2 [a]	288 [a]	7.35
Carbopl 941 concentration, %			
1	3.08 (0.763)	10.2 (2.13)	7.53 (2.90)
2	5.61 (1.25)	21.5 (4.24)	7.50 (2.75)
3	8.63 (1.87)	35.7 (6.74)	7.45 (2.45)
4	12.9	53.6	7.38
5	16.7 (4.19)	72.3 (19.0)	7.30 (2.40)
6	22.2	107	7.40
7	29.6 [a]	137	7.33
8	36.9 [a]	178	7.28
9	43.8 [a]	212	7.30
10	67.0 [a]	318 [a]	7.60

[a] Values obtained using the small cone.

infinite number of Voigt units, but only three were required to reproduce the creep curve, which was represented by the equation

$$J(t) = J_0 + \sum_{n=1}^{3} J_n(1 - e^{-t/\tau_n}) + \frac{t}{\eta_d} \qquad (1)$$

where J(t) = total creep compliance at time t, J is the ratio of shear strain to shear stress, J_0 = residual shear compliance, J_1, J_2, J_3 = shear compliances of elastic parts of Voigt Units 1, 2, 3, respectively, τ_1, τ_2, τ_3 = retardation times of Voigt Units 1, 2, 3, respectively and η_0 = residual shear viscosity.

To check the accuracy of Eqn 1 a computer program was employed to reconstitute the original creep curve with the derived parameters as input data. The discrete spectral analysis was accepted if the reconstituted curve was within 2% of the experimental curve.

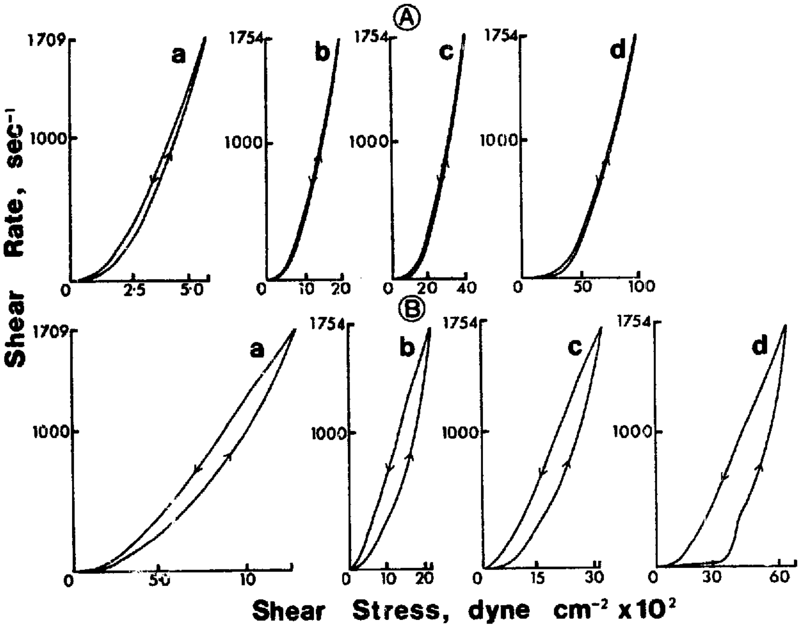

Fig. 4. Flow curves for unneutralized gels containing different amounts of (A) Carbopol 940 and (B) Carbopol 941 obtained using the high shear rate regime. a: 1%; b: 2%; c: 3%; d: 5%.

The behaviour of the shear compliance after 50 min (J_{50}), J_0 and η_0 versus polymer concentration are in Fig. 6 and numerical data, including time dependent data, are in Table 5.

TABLE 3

APPARENT ACTIVATION ENERGIES FOR VISCOUS FLOW FOR 1% AND 3% NEUTRALIZED AND UNNEUTRALIZED CARBOPOL 940 AND 941 GELS

a = Values derived from data obtained with the high shear rate regime; b = Values derived from data obtained with the low shear rate regime; c = Values derived from data obtained from creep tests. Figures in parentheses are the correlation coefficients for the relevant plots.

Neutralized systems	Apparent activation energy for viscous flow, kcal mol^{-1}		
	a	b	c
1% Carbopol 940	1.53 (0.996)	1.46 (0.998)	7.26 (0.999)
3% Carbopol 940	1.59 (0.994)	1.52 (0.998)	7.59 (0.999)
1% Carbopol 941	1.57 (0.999)	2.27 (0.999)	3.73 (0.999)
3% Carbopol 941	1.40 (0.998)	1.70 (0.999)	1.73 (0.983)
Unneutralized systems	a	b	c
1% Carbopol 941	1.05 (0.959)	1.10 (0.939)	
3% Carbopol 941	0.762 (0.986)	1.03 (0.984)	

TABLE 4

APPARENT VISCOSITIES, OBTAINED WITH THE HIGH SHEAR RATE REGIME, AND pH VALUES FOR 3% NEUTRALIZED AND UNNEUTRALIZED CARBOPOL 940 AND 941 GELS CONTAINING DIFFERENT SOLVENTS AND FOR 3% GELS NEUTRALIZED WITH DIFFERENT BASES

Solvent/polymer or neutralizer/polymer system		Apparent viscosity, poise	pH
Carbopol 940 +:	(neutralized)	34.3 [a]	8.1
ethylene glycol	(unneutralized)	17.6	3.1
	(neutralized)	24.0 [a]	8.1
propylene glycol	(unneutralized)	25.8 [a]	3.3
	(neutralized)	152 [a]	7.7
glycerin	(unneutralized)	68.8 [a]	2.9
Carbopol 941 +:	(neutralized)	20.2	8.1
ethylene glycol	(unneutralized)	13.4	3.0
	(neutralized)	12.7 [a]	8.1
propylene glycol	(unneutralized)	17.3	3.4
	(neutralized)	94.0 [a]	7.7
glycerin	(unneutralized)	43.1 [a]	2.7
Carbopol 940 +:			
ethanolamine		12.3	7.7
diethanolamine		13.2	7.7
triethanolamine		12.5	7.4
sodium hydroxide		11.2	7.0
Carbopol 941 + :			
ethanolamine		8.28	7.5
diethanolamine		9.22	7.9
triethanolamine		8.63	7.4
sodium hydroxide		7.48	7.2

[a] Values obtained with small cone.

For the unneutralized gels the creep compliance results were represented by a 6-element mechanical model (a Maxwell unit in series with two Voigt units). Graphical analyses results are in Table 6. The consistencies of 1% unneutralized gels were too low to achieve a steady base line and these gels were not tested.

Neutralized 3% gels were examined in creep at 10, 20 and 50°C. Increased temperature reduced the consistencies of the gels as indicated by increased residual compliance and decreased residual viscosities. Residual viscosities were used in Arrhenius-type plots and apparent activation energies for viscous flow derived from these plots are in Table 3.

Creep curves obtained for gels containing different non-aqueous solvents indicated increased consistency compared with data for aqueous systems. Data for systems neutralized with different bases did not indicate a definite trend. The relative contributions of J_0, J_{50}, and η_0 to the consistency of Carbopol gels containing different solvents and neutralizers are in Fig. 7 and Fig. 8. The 100% glycerin systems were not tested because their consistencies were so high that it was difficult to load the viscometer and obtain a steady base line.

TABLE 5

DISCRETE VISCOELASTIC PARAMETERS DERIVED FROM CREEP CURVES FOR NEUTRALIZED CARBOPOL 940 AND 941 GELS

		Carbopol 940									
		1%	2%	3%	4%	5%	6%	7%	8%	9%	10%
Compliance, dyne^{-1} cm^2 × 10^{-6}	J_0	186	166	145	120	97.4	87.5	78.6	65.0	58.0	50.1
	J_{50}	243	223	188	158	130	117	105	93.2	82.0	75.7
	J_1	12.4	10.5	10.3	9.44	13.7	9.12	8.78	7.11	8.32	7.65
	J_2	8.87	10.3	9.78	6.78	4.75	5.44	3.75	5.51	3.10	3.63
	J_3	21.2	20.2	14.6	12.5	9.25	8.28	8.45	8.72	7.83	8.76
Retardation time, s	τ_1	1020	1080	1050	1030	1100	1050	1100	1110	1130	1140
	τ_2	134	137	142	133	137	134	129	138	133	138
	τ_3	15.4	23.3	18.4	17.6	23.6	20.0	19.8	16.5	19.1	18.8
Viscosity, poise × 10^7	η_0	23.4	25.3	30.3	35.7	36.2	40.5	45.5	46.6	51.8	52.0
	η_1	8.25	10.3	10.2	10.9	7.99	11.5	12.5	15.5	13.5	14.9
	η_2	1.51	1.34	1.76	1.28	2.89	2.45	3.44	2.49	4.27	3.82
	η_3	0.0726	0.115	0.126	0.141	0.255	0.242	0.234	0.189	0.244	0.214

		Carbopol 941									
		1%	2%	3%	4%	5%	6%	7%	8%	9%	10%
Compliance, dyne^{-1} cm^2 × 10^{-4}	J_0	24.5	16.0	10.8	8.07	5.37	3.68	3.05	2.43	1.70	1.48
	J_{50}	41.0	29.4	23.0	16.9	11.4	8.95	7.74	5.87	4.92	4.04
	J_1	3.58	4.54	4.17	2.42	1.75	1.10	1.20	0.986	1.39	0.764
	J_2	2.80	2.16	1.28	1.25	1.08	1.09	0.877	0.775	0.602	0.626
	J_3	5.98	2.90	4.04	2.65	2.21	1.68	1.45	1.14	1.14	0.722
Retardation time, s	τ_1	864	1100	1020	938	1060	885	929	1060	1150	974
	τ_2	143	153	136	146	144	202	143	154	136	142
	τ_3	18.6	21.5	18.5	18.7	18.3	27.7	21.9	22.5	24.3	21.9
Viscosity, poise × 10^5	η_0	60.2	63.3	85.3	108	190	213	219	362	354	443
	η_1	24.1	24.2	24.5	38.7	60.9	80.4	77.7	107	82.7	127
	η_2	5.11	7.10	10.6	11.6	13.4	18.6	17.3	19.8	22.6	22.6
	η_3	0.311	0.74	0.416	0.706	0.828	1.65	1.50	1.97	2.12	3.30

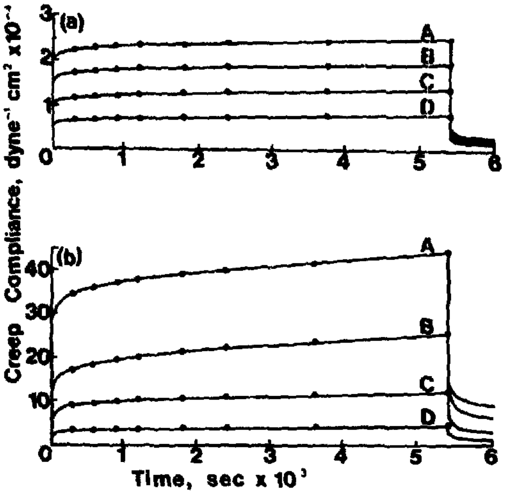

Fig. 5. Creep compliance curves for neutralized Carbopol 940 gels (a) and 941 gels (b). Circles represent data reconstituted from the creep equation. A: 1%; B: 3%; C: 5%; D: 10%.

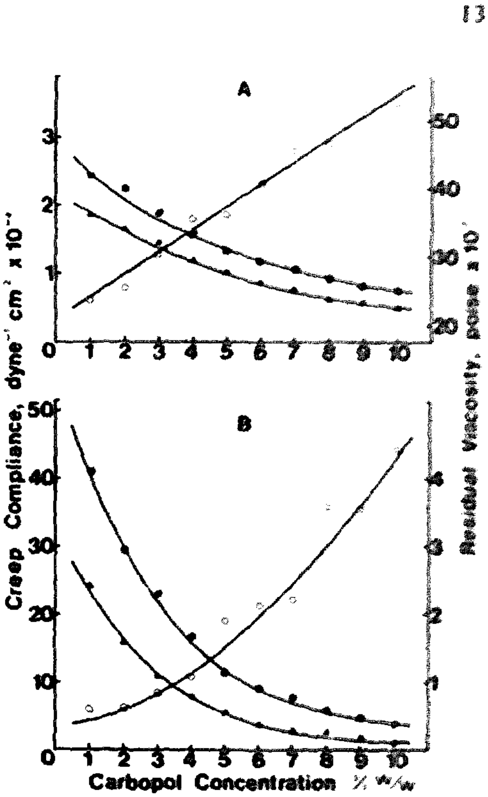

Fig. 6. Residual compliance (▲), compliance after 50 minutes (●) and residual viscosity (○) for neutralized Carbopol 940 gels (A) and 941 gels (B).

TABLE 6

DISCRETE VISCOELASTIC PARAMETERS DERIVED FROM CREEP TESTS ON UNNEUTRALIZED CARBOPOL 940 AND 941 GELS

		Carbopol 940			Carbopol 941		
		2%	3%	5%	2%	3%	5%
Compliance, dyne^{-1} cm^2 × 10^{-6}	J_0	313	200	92.3	1080	978	423
	J_1	9.50	12.8	4.38	109	144	63.3
	J_2	0.216	12.1	8.17	150	161	56.2
Retardation time, s	τ_1	828	357	448	736	537	479
	τ_2	6.80	17.8	33.3	42.5	34.7	77.4
Viscosity, poise × 10^6	η_1	87.1	27.8	102	6.74	3.72	7.57
	η_2	0.314	1.48	0.407	0.283	0.215	0.138
	η_0	312	388	661	39.5	51.9	55.6

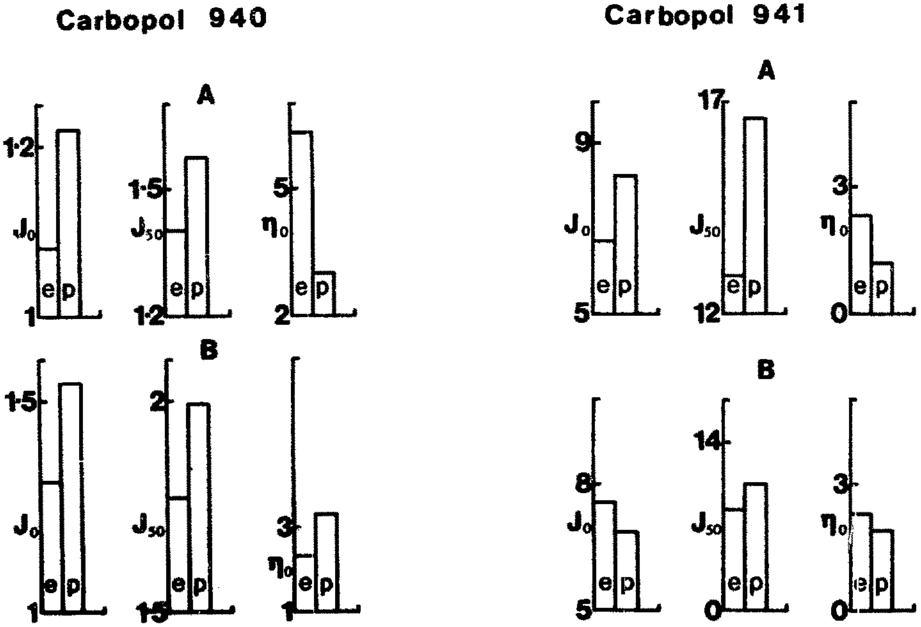

Fig. 7. Variation of J_0, J_{50} (dyne^{-1} cm^2 × 10^{-4}) and η_0 (poise × 10^7) for 3% Carbopol 940 and 941 gels containing 100% non-aqueous solvents, neutralized (A) and unneutralized (B). e = ethylene glycol; p = propylene glycol.

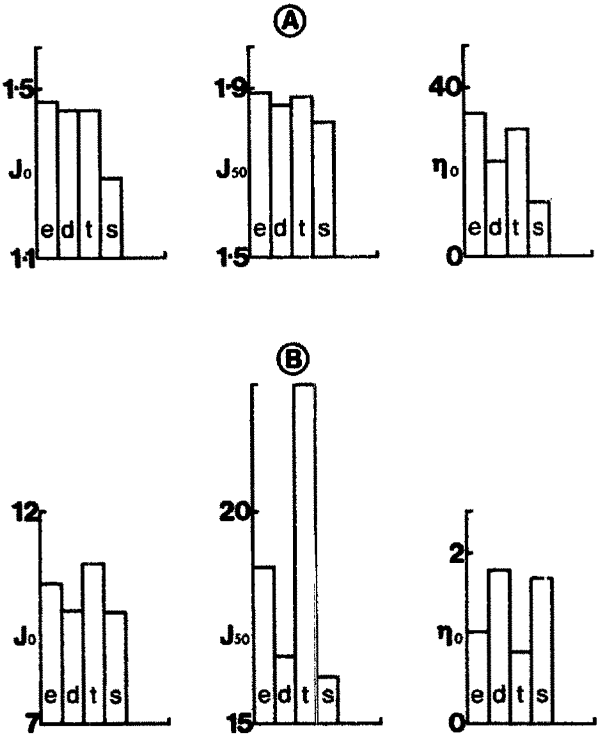

Fig. 8. Variation of J_0, J_{50} (dyne^{-1} cm^2 × 10^{-4}) and η_0 (poise × 10^7) for 3% Carbopol 940 gels (A) and Carbopol 941 gels (B) neutralized with different bases. e = ethanolamine; d = diethanolamine; t = triethanolamine; s = sodium hydroxide.

DISCUSSION

The typical pharmaceutical working procedure employed here had no appreciable effects on the continuous shear properties of neutralized Carbopol 940 gels. This indicates that either disrupted gel structure reforms very quickly or that no structure breakdown occurs under these shearing conditions. As little or no hysteresis was shown by the flow curves for these gels the latter explanation seems more likely. For neutralized Carbopol 941 gels milling caused some structure breakdown within the gel which was indicated by a decrease in the values of apparent viscosity. The structure of both types of gels is partially due to hydrogen bonding which may make a more significant contribution to the structure of the Carbopol 941 gels than to the Carbopol 940 gels. The decrease in apparent viscosity of the Carbopol 941 gels would then be explained by the disruption of hydrogen bonding during the milling process.

Both types of unneutralized gels showed larger reductions in apparent viscosity when compared with their neutralized forms. This is consistent with the theory that the structure of the unneutralized systems is primarily due to hydrogen bonding (Dittmar, 1957; Lang, 1972) which is easily destroyed by shear.

This test shows that the neutralized systems can withstand relatively high rates of shear without serious loss of consistency. This property would have industrial importance in the design of gel products containing drugs or other solid materials incorporated into the gel base by a milling or homogenizing process. The shear thinning effect is more prominent with the unneutralized systems than with the neutralized systems. However, further work would be necessary to assess the significance of this effect, i.e. whether the structure reforms and if the milled material is neutralized how does its consistency compare with material that is milled after neutralization? This is also relevant to industrial processes where there would be a lower energy requirement for milling unneutralized rather than neutralized material.

The curves in Fig. 1a and b show that both types of gel behave similarly with respect to neutralizer concentration. In terms of the thickening mechanism the behaviour indicated by the apparent viscosity curve is due to uncoiling of the polymer molecules to form either rigid chains (Dittmar, 1957; Fischer et al., 1961) or discrete swollen gel particles (Taylor and Bagley, 1975). Above 25–30% triethanolamine the apparent viscosities begin to increase more rapidly although the pH hardly changes. At these concentrations the excess amine acts as a solvent rather than a neutralizing agent and the increased resistance to flow is due to the increased viscosity of the continuous phase and electrostatic association of the amine and polymer molecules. The presence of this weak electrostatic association, which is destroyed by shear, is shown rheologically by a gradual increase in the hysteresis loop area of the flow curves obtained for gels containing more than 25% triethanolamine.

The manufacturers quote an equivalent weight of 75 for the Carbopol polymers. For the 3% gel studied here 6% amine would be required to neutralize the gels. This agrees with the pH curves since 6% amine corresponds approximately to neutrality (experimental pH 7.3) and to the point where the gradient of the curve decreases rapidly. This concentration of amine also corresponds to the portion of the apparent viscosity curve where its gradient begins to decrease, thus *slight* errors in the amount of amine added would have a relatively small effect on the apparent viscosity of the system.

This test illustrates two differences between Carbopol 940 and 941; Carbopol 941 is a less efficient thickening agent than Carbopol 940 and the increase in consistency, on raising the pH (increase in amine concentration), is less rapid for Carbopol 941 gels than for Carbopol 940 gels. The test also shows that the equivalent weight given by the manufacturers is sufficiently accurate for the preparation of neutral gels. However, unlike neutralization with strong bases, where addition of excess base causes thinning, successive additions of amine produce successive increases in the apparent viscosities of both types of gels.

The change in apparent viscosity over 6 weeks for the Carbopol 940 gels was small. These systems were therefore considered stable with respect to time. During the storage period the gels exhibited slight syneresis which would account for the small increase in apparent viscosity. Carbopol 941 gels, particularly those unneutralized, demonstrated a decrease in consistency (probably due to polymer degradation) over the test period. For both Carbopol 940 and 941 the consistencies of the unneutralised gels changed more than those of the neutralized gels showing that the hydrogen bonded systems were less stable than the chemically bonded systems.

When the consistencies of the gels were compared over the 2–8 day storage period a change of 1% or less was observed. Therefore, in order to minimize time effects this storage period was adopted for all subsequent tests, i.e. gels were manufactured and stored in the dark for at least two days and tested within 8 days of preparation.

However, the systems stored in daylight exhibited marked photodegradation. Morimoto and Suzuki (1972) investigated the photodegradation of poly(alkyl acrylates), which are similar to Carbopols, and suggested that the mechanism for this process was side group scission followed by the formation of either cross-links or conjugate bonds; this reduces the molecular size of the polymers and hence the consistency of the gels. These authors note that mobility of the polymer chains would influence the photodegradation mechanism and this is consistent with the experimental data given here because the neutralized Carbopol 940 gel, which initially was the most rigid, shows the smallest decrease in consistency and the least rigid gel., i.e. unneutralized Carbopol 941 exhibits the largest loss in consistency. These authors also suggest that the formation of conjugate bonds causes the gradual yellowing observed in polyacrylate and Carbopol gels. However, the neutralized systems yellowed faster and more intensely than the unneutralized systems and thus it seems probable that this process is also due to oxidation of the amine.

This behavior suggests light-resistant containers or stabilizing agents (e.g. alcohols, polyhydroxy compounds and chelating agents) for Carbopol-based pharmaceutical or cosmetic products. Schwarz and Levy (1958) investigated the effect of daylight on the consistency of Carbopol 934 gels containing stabilizing agents and Adams and Davis (1973) found that 3–10% ethanol reduced the consistency loss of gamma-irradiated 1% gels of each grade of Carbopol to 20%.

During temperature cycling gels exhibited syneresis which was enhanced by the test conditions because, at 40°C, water evaporated from the gel into the free space of the container. When the gels were stored at 3°C the water vapour condensed and was only partially absorbed and then only into the upper layers of the gel. This process accounts for the increase in apparent viscosity observed during the cycles.

From this test it can be inferred that water is more strongly bound (or trapped) in the neutralized systems than in the unneutralized systems and thus the neutralized gels are more stable to temperature variation than the unneutralized systems.

The flow curves for both types of Carbopols (Figs. 2 and 3) were similar and they all demonstrated the presence of a yield value. The ability of this material to sustain a relatively high shear stress without exhibiting significant flow can be used in the preparation of suspensions. Yield values for Carbopol gels were investigated by Fischer et al. (1961) who found that the value depended on polymer concentration and pH and that it was independent of the stress applied to the systems. These authors suggested that the presence of a yield value was due to chain branching on the polymer molecule. The unneutralized gels, which were much lower in consistency than the neutralized systems, also exhibited plastic flow (Fig. 4). However, unneutralized Carbopol 941 gels, unlike the other gels, exhibited significant hysteresis. This was attributed to increased hydrogen bonding which produced a relatively weak network structure within the gel.

The exponential relationship between apparent viscosity and polymer concentration, which is typical of high molecular weight polymer systems (Alexander and Johnson, 1949; Martin et al., 1964; Sherman, 1970) was examined for the best straight line fit, according to the least squares criterion. The following relationships were assessed: linear apparent viscosity and linear concentration; log apparent viscosity and linear concentration; log apparent viscosity and log concentration; linear apparent viscosity and log concentration. For Carbopol 940 gels the log apparent viscosity and linear concentration relationship produced the best straight line. The data for Carbopol 941 gels was equally well represented by the log apparent viscosity/linear concentration and the log apparent viscosity/log concentration relationships and in neither case was the correlation as good as that obtained for the Carbopol 940 data. These relationships can be expressed by:

$$\log \eta_a = K_1C + B_1 \tag{2}$$

$$\log \eta_a = K_2\log C + B_2 \tag{3}$$

where η_a = apparent viscosity, C = polymer concentration, and K_1, B_1, K_2, B_2 = constants. The value of these constants for Carbopol 940 and 941 are given in Table 7. Thus by substituting these constants into Eqns. 2 and 3 it is possible to predict the approximate concentration of Carbopol required to produce a given apparent viscosity or vice versa. However the use of these equations is limited because, as can be seen from Table 7, the constants are characteristic of the type of Carbopol and are shear dependent and, therefore, when used for predictive work, they could only be applied under specific rheological conditions.

The apparent viscosity data derived from the high shear rate regime indicated that the Carbopol 940 gels were of higher consistency than comparable Carbopol 941 gels up to 10% polymer concentration where the positions were reversed. The low shear rate regime data showed a similar trend only up to 5% polymer concentration. At 6–9% polymer concentration the apparent viscosities were similar for both types of gel and at 10% polymer the apparent viscosity for Carbopol 941 was higher than that for Carbopol 940. These results did not appear to depend on the pH of the system as this remained rela-

TABLE 7

VALUES OF THE CONSTANTS K_1, B_1, K_2 and B_2 OBTAINED FROM A LEAST SQUARES ANALYSIS OF THE APPARENT VISCOSITY/CONCENTRATION DATA USING EQNS. 2 AND 3

a = data for high shear rate regime; b = data for low shear rate regime; c.c. = the correlation coefficient.

System		Constants					
		K_1	B_1	c.c.	K_2	B_2	c.c.
Carbopol 940	a	0.111	2.76	0.992	–	–	–
	b	0.117	3.33	0.996	–	–	–
Carbopol 941	a	0.136	2.50	0.987	1.29	2.40	0.986
	b	0.153	3.05	0.984	1.47	2.93	0.990

tively constant for both types of gels and throughout the concentration range (Table 2). Two factors can account for this behaviour. Firstly, at low shear rates relatively little structure breakdown (or possibly molecular orientation) occurs and within certain concentration limits both polymers behave similarly and secondly, at 10% Carbopol concentration there may be insufficient solvent to solvate Carbopol 940 but sufficient to solvate the Carbopol 941; thus Carbopol 940 would not show the expected increase in apparent viscosity. For the 1% unneutralized gels Carbopol 941 exhibited a higher apparent viscosity than Carbopol 940, at 2% polymer concentration the values were similar and at 3% polymer concentration their relative positions were reversed. As demonstrated by the neutralized systems the relative changes in apparent viscosity were not due to pH because although the pH decreased with increase in polymer concentration similar values were obtained for both types of Carbopol (Table 2). This behaviour can be explained by assuming that molecular orientation, and therefore hydrogen bonding is more pronounced for Carbopol 941 at low concentrations than for Carbopol 940. However at higher concentrations the polymer molecules are less easily orientated and hydrogen bonding makes a less significant contribution to the overall consistency of the systems.

The modification of the Arrhenius equation used here to describe the behaviour of the apparent viscosity/temperature data had the form:

$$\eta_a = Ke^{(E/RT)} \tag{4}$$

where η_a = apparent viscosity, K and E = constants, R = gas constant and T = absolute temperature. Eqn. 4 was also derived for viscosity at low stresses (Eyring, 1956) based on the theory of rate processes for viscous flow (Glasstone et al., 1941). The Maxwell–Boltzmann distribution law indicates that E is equivalent to an activation energy for viscous flow and given units of calories per mol.

The apparent activation energies for flow for the neutralized Carbopol 940 gels were relatively constant at both concentrations and for both shear rate regimes (Table 3). The low values of E indicate that the apparent viscosities of the systems are not greatly affected by temperature change. For Carbopol 941 gels the value of E, although of the same order as those obtained for Carbopol 940, were more variable and appeared to depend on both polymer concentration and shear rate. This may be due to a component of the gel structure (e.g. hydrogen bonding) being more prominent in Carbopol 941 gels than in Carbopol 940 gels. This explanation would also apply to values of E obtained for the unneutralized Carbopol 941 gels. These values were lower than those obtained for the neutralized gels which indicates greater thermal stability. Fischer et al., (1961) obtained similar values of E at several pH values and found that decreasing the pH increased E. Although the magnitudes of E obtained by these authors were similar to those given above the opposite behaviour with respect to pH was observed.

The behaviour of the unneutralized Carbopol 940 gels and Carbopol 941 gels, below 25°C, resulted from changes in the degree of solvation and/or molecular shape of the polymer. This was caused by either temperature variation or shear processing or a combination of both factors (Alexander and Johnson, 1949; Martin et al., 1964).

Although the Arrhenius equation was used by several workers (e.g Fischer et al., 1961; Lenk, 1965; Davis, 1969a) there is some controversy concerning the activation energies derived from it as the equation contains no term involving free volume change with temperature (Jobling, 1953: Bondi, 1956). Despite this criticism the activation energies were useful in characterizing the systems because they are concerned with the energy necessary to cause the individual components of a system to move from one equilibrium position to another in the direction of flow (Barry and Grace, 1970).

For the unneutralized systems containing 100% non-aqueous solvent the apparent viscosities decreased with decrease in solvent molecule size. This behaviour paralleled the order of viscosities of the solvents themselves, which were glycerin 16.9 poise, propylene glycol 0.553 poise and ethylene glycol 0.171 poise. (Solvent viscosities were obtained using the Ferranti–Shirley viscometer in the non-automatic mode at 25 ± 0.1°C.) However, for the neutralized systems this order was changed so that the ethylene glycol systems remained lower in consistency than the glycerin systems but were higher in consistency than the propylene glycol systems.

This change in behaviour is probably caused by changes in solvation and/or molecular shape (Alexander and Johnson, 1949). If a solvent has a strong affinity for a solute then strong solvation will occur and this will tend to uncoil a previously curled-up chain making it more accessible to the solvent. However, if no such affinity exists the macromolecule will tend to remain curled. Thus in the systems containing 100% non-aqueous solvent glycerin is the best solvent (or possesses maximum affinity for the solute) in both neutralized and unneutralized conditions; ethylene glycol is a better solvent than propylene glycol in neutralized conditions and the reverse is true for unneutralized conditions. The component of the consistency derived from solvation effects is more susceptible to shear breakdown than that produced by chemical means (i.e. neutralization) and this is indicated in the flow curves by an increase in hysteresis loop area (Martin et al., 1964).

These results illustrate the large range of apparent viscosities and types of preparations that can be obtained by using hydroxylated organic solvents and that the consistencies depend more on the nature of the solvent than on its molecular size and inherent viscosity.

The relatively small differences in consistency shown by the gels containing different neutralizers was due to differences in the pH (Table 4) and steric effects. The pH differences may have been due to small errors in the amount of base added or to the relatively large amine molecules preventing complete neutralization of the carboxyl groups and therefore remaining in solution. The organic amines will have a much greater effect on the molecular size of the neutralized polymer than sodium ions and this will tend to produce gels of higher consistency. However, the information obtained here suggests that from a pharmaceutical formulation aspect the choice of neutralizer could be primarily made on physiological and compatibility grounds.

Simple mechanical models produced by combining Hookean springs and Newtonian dashpots were used here to simulate viscoelastic behaviour. Such model representation is convenient when visualizing solid-like and liquid-like properties of real materials but does not necessarily imply anything about underlying molecular mechanisms, nor is it essential to the development of viscoelastic theory. The models are simple representations of equations of flow and a particular experimental system may be described by several equivalent models whose moduli may be interrelated (Kuhn, 1947; Alfrey, 1948; Bland, 1960). However, the individual elements of a model may be qualitatively identified with general processes at a molecular level (Alfrey and Gurnee, 1956). Thus, the instantaneous elastic component, which provides the residual compliance, simulates the elasticity of the gel structure and is associated with bond stretching.

The viscoelastic region, represented by Voigt units connected in series, is associated with the elongation and orientation of the polymer chains which involve the breaking and reforming of secondary bonds. The retardation time is the time taken to break and reform such secondary bonds or alternatively the time taken by the polymer chains to reach their new equilibrium orientation. These processes do not all occur at the same rate and thus a spectrum of retardation times exists. However, for reasons given below, all creep results were analyzed into discrete spectra. This has the effect of grouping similar retardation times (processes) into discrete average values. After sufficient time at constant stress (i.e. when all Voigt units were fully extended) further deformation was caused by viscous flow which is represented by the residual dashpot. On a molecular level this can be interpreted as the slippage of polymer chains past one another. This residual viscosity indicates that, provided the time scale is long enough, the material will flow (i.e. Carbopol gels do not possess *true* yield values).

The creep curves for both types of Carbopol gels (Fig. 5) show predominant elastic behaviour with high residual viscosities and relatively restricted viscoelastic regions. J_0 for 1% Carbopol 940 and 941 gels respectively, represents 76% and 60% of J_{50}, and for 10% Carbopol 940 and 941 gels it accounts for 66% and 37% of J_{50}. This characteristic together with the high values of η_0 indicates that these systems approximate reasonably closely to elastic solids; certainly they are more like true solids than other pharmaceutical systems such as o/w and w/o creams.

The graphical methods of analysis for the creep curves involve plotting the difference between experimentally obtained lines and extrapolated lines. Due to the dominant elastic nature of the materials these differences are relatively small. Thus small errors in measuring such differences may significantly affect the accuracy of the derived parameters. Further errors would be incurred when determining the gradient of the linear portion of the creep curve. This section, particularly with Carbopol 940 gels, was nearly horizontal and thus small differences in the measured gradient would have a relatively large effect on the derived strain rate. The relatively restricted viscoelastic region of the curve prevented an accurate continuous retardation spectral analysis; only discrete retardation times were derived.

As the above behaviour suggests that the analytical method was used close to its limits of accuracy, the following discussion will concern general trends and occasional exceptions to these trends will not be considered significant.

When J_0 and J_{50} were plotted against polymer concentration typical exponential curves were obtained (Fig. 6). A similar trend was observed with the continuous shear results. An exponential relationship between η_0 and concentration was observed for Carbopol 941 gels and a linear relationship was observed for Carbopol 940 gels, although data were scattered. However, the significance of this rheological variation was not certain.

The compliance/concentration data were examined for the best straight line fit using the method described for the continuous shear data. For both types of gel the best straight line was obtained using the log compliance and linear concentration relationship (cf. Eqn. 2):

$$\log J_0 \text{ or } \log J_{50} = KC + B \qquad (5)$$

where C = polymer concentration, and K, B = constants.

Although the constants differ for the two types of Carbopols they are similar for each gel type when either J_0 or J_{50} are used. This is a further indication of the prominent elastic character of the gels. The least squares analysis of the compliance data provides an improved straight line fit (i.e. a higher correlation coefficient) compared with a similar analysis on apparent viscosity data. Furthermore, Eqn. 5 has the advantage of using fundamental data which are independent of shear rate provided that data are gathered in the linear region. Thus, relatively accurate prediction of the compliance/concentration relationship is possible. This has a practical significance when compliance or polymer concentration are related to formulation parameters such as spreadability, suspending ability or bioavailability.

Carbopol 940 gels possessed lower residual and Voigt compliances and higher residual

TABLE 8

VALUES FOR THE CONSTANTS K AND B OBTAINED FROM A LEAST SQUARES ANALYSIS OF THE LOG COMPLIANCE VERSUS LINEAR CONCENTRATION RELATIONSHIP FOR NEUTRALIZED CARBOPOL 940 AND 941 GELS

c.c. = correlation coefficient; J_0 and J_{50} are the shear compliances (dyne^{-1} cm^2) at zero time and 50 min.

System		K	B	c.c
Carbopol 940	J_0	−0.0646	−3.66	0.998
	J_{50}	−0.0588	−3.56	0.995
Carbopol 941	J_0	−0.0136	−2.54	0.994
	J_{50}	−0.0113	−2.32	0.994

and Voigt viscosities than Carbopol 941 gels of the same concentration (Table 5). The retardation times for both types of gels were similar and did not change markedly over the concentration range. This suggests that the nature of the secondary bonds was similar although the number probably varied. The difference in compliance between Carbapol 940 and 941 gels diminished with increased polymer concentration. However, the fundamental data did not show the relative consistency cross-over indicated by continuous shear results. Thus, the results of the destructive continuous shear tests do not represent the true rheological difference between the two systems. A similar difference in behaviour was observed for the unneutralized gels. For these systems fundamental data, unlike the continuous shear results, indicated that unneutralized Carbapol 940 gels possessed a higher consistency (higher viscosities and lower compliances) than unneutralized Carbopol 941 gels at all concentrations.

The creep curves for the unneutralized systems had a shorter viscoelastic portion compared with the neutralized systems. Thus, these systems approximate more closely to elastic solids and were satisfactorily represented by two Voigt units (Table 6). The fundamental data did not show the large consistency difference between comparable unneutralized and neutralized systems which was indicated by the continuous shear results (Table 4). For the 2% and 3% Carbopol 940 systems J_0 for the unneutralized gels were higher than for the neutralized gels but for both these concentrations the values of η_0 were lower for the latter than for the former. The 5% unneutralized Carbopol 940 gel exhibited a lower J_0 and a higher η_0 than the 5% neutralized system; η_0 for the unneutralized system was higher than that obtained for the 10% neutralized gel. For the 2, 3 and 5% unneutralized Carbopol 941 gels values of J_0 were lower than those for the comparable neutralized systems and the values of η_0 were higher. For this type of Carbopol η_0 for both the 3% and 5% unneutralized gels was higher than that obtained for the 10% neutralized gel.

The retardation times of Voigt units one and two for the unneutralized systems are shorter than those for the neutralized systems which indicates that the nature of the secondary bonds is different in the neutralized and unneutralized states. Unlike the neutralized systems the retardation times for the unneutralized gels are not constant. For Voigt unit one they tend to decrease with increased concentration and for Voigt unit two they tend to increase with increased concentration. This shows that the character rather than the number of the two types of secondary bonds change with concentration. However, a more detailed interpretation is not practical because only three concentrations were tested and as discussed above the viscoelastic parameters can be associated with relatively large errors.

The behaviour described above illustrates the possible shortcomings of continuous shear experiments. Consistency differences exhibited in continuous shear tests were reversed when the gels were examined in their rheological ground state. The behaviour of materials at low shear rates would have particular significance in formulations such as suspensions and emulsions and for these examples continuous shear results could be misleading.

The Arrhenius-type equation used for the creep data was the same as Eqn. 4 except that η_0 substituted for apparent viscosities. The activation energies for flow (E) for neutralized Carbopol 940 gels were similar for both concentrations and markedly higher than the values obtained with the apparent viscosity data. Glasstone (1956) indicated that E depended on the size of the flowing particles. Larger entities meet a higher potential energy barrier to flow and thus need a higher activation energy. The results for Carbopol 940 suggest that in creep the flowing particles are larger than in continuous shear tests. For Carbopol 941 gels the values of E were markedly lower than those for Carbopol 940 gels and, unlike the latter, depended on polymer concentration. For 3% Carbopol 941 gels the value of E derived from the residual viscosity data was larger than the value derived from the apparent viscosity data. However, for the 1% Carbopol 941 gel the values of E derived from both sets of data were similar. This suggests that in creep the flowing particles of Carbopol 941 gels, at both concentrations, are smaller than those in Carbopol 940 gels. Comparison of the values of E derived from the residual viscosity data and the apparent viscosity data indicates that for the 3% Carbopol 941 gel the flowing particles are larger in creep than in continuous shear and for the 1% Carbopol 941 gel the particles are similar in size. As previously suggested, this variation in E may be due to a component of the gel structure, such as hydrogen bonds, being more pronounced in Carbopol 941 gels than in Carbopol 940 gels. However, the qualitative comparisons made here are only tentative because the values of E derived from continuous shear viscometry were overall averages which depended on the material and the method of testing.

It can be seen from Fig. 7 that the values of J_0, J_{50}, and η_0 for the neutralized gels containing non-aqueous solvents showed the same consistency trends as indicated by the apparent viscosity data (Table 4). However, for the unneutralized systems only partial agreement between a particular viscoelastic parameter and the continuous shear results was observed.

The values of J_0 and J_{50} for 3% aqueous systems were higher than those for comparable gels containing organic solvents. However, the values of η_0 did not show a consistent trend when organic solvents were included in the systems, nor when these systems were neutralized. These results indicate that the solvent predominantly affects the elastic and retarded elastic properties of the gels and has a variable effect on η_0.

The variation of J_0, J_{50} and η_0 for 3% gels neutralized with different bases is shown in Fig. 8. These data did not show any particular trend nor did they agree with the consistency order indicated by the continuous shear results. Thus, the effect of different neutralizers cannot be predicted and from a consumer viewpoint they could be selected for practical reasons alone.

In general the continuous shear results indicated that Carbapol 940 forms gels of higher consistency than Carbapol 941 and the consistencies of both types of gels depend on polymer concentration, pH and solvent. The differences in consistencies between the two types of polymer were confirmed by viscoelastic techniques which also indicated that to the first approximation Carbopol gels could be considered as elastic solids. The gels exhibited a relatively small variation in consistency with temperature and were almost unaffected by milling, temperature cycling and ageing. The use of organic solvents increased the range of rheological properties that may be obtained with Carbopol gels and, as indicated by the continuous shear results, the fundamental properties are not related to the inherent viscosities of the solvents but to some other property such as solvating or hydrogen bonding ability. The results indicate that the contributions of the elastic and viscous elements to the overall consistency of the gels can only be accurately described by viscoelastic data and that the trends shown by these data do not necessarily agree with the average results obtained from continuous shear experiments. Thus, as previously indicated for the aqueous gels, the destructive tests may provide misleading data on the fundamental nature of the materials.

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