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Rheological synergism between ionic and non-ionic cellulose gums

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Summary

The rheological properties of 50:50 mixtures of an ionic (sodium carboxymethylcellulose (NaCMC)) and various non-ionic cellulose gum solutions have been assessed using a rotational cup and bob viscometer and the apparent viscosities at each shear rate compared with their calculated mean. All the non-ionic celluloses studied gave an increase in viscosity over the calculated value.

The greatest increase in viscosity was exhibited by a combination of methylcellulose (MC) with NaCMC and an optimum viscosity grade (≡ chain length) of HPMC was found.

The interaction of xanthan gum with NaCMC was also investigated and they were shown to be incompatible.

The mechanisms by which synergism occurs is discussed at the molecular level in relation to side chain configuration, degree of substitution cross linking and polymer chain length. The combination of an ionic (NaCMC) and a non-ionic cellulose gum produces an increased viscosity due to cross-linking and allows the use of cellulose gums at reduced concentrations in formulated products.

Introduction

Cellulose gums are widely used in the food and pharmaceutical industries as thickening, stabilizing and emulsifying agents and some have found use as tablet

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binders and in sustained release preparations. Many workers have extensively studied the properties of ionic and non-ionic cellulose gums in solution and with various electrolytes (Allgen and Roswall, 1954; Levy, 1961; Brown and Henley, 1964; Storz et al., 1965a; Storz et al., 1965b; Kassem and Mattha, 1970a and b; Rees, 1972). However, potential interactions between ionic and non-ionic gums has received little attention although synergistic viscosity behaviour has been briefly described in the technical literature for sodium carboxymethylcellulose (Hercules Powder Company, 1976) and xanthan gum (Kelco Company, 1978).

The purpose of the present work was therefore to investigate the rheological synergism between sodium carboxymethylcellulose and non-ionic cellulose gums and the mechanisms by which this occurs. An enhancement of apparent viscosity by this approach allows viscosity adjustments using gums at reduced levels. This increases the cosmetic acceptability, palatability and cost effectiveness of formulated products and may reduce the inactivation of preservatives reported for cellulose gums (Tillmann and Kuramoto, 1957; Miyawaki, 1959; Deluca and Kostenbauder, 1960).

Materials and methods

Materials

The materials used in this study are shown in Table 1. They were used as received.

Methods

(1) Preparation of gum solutions. Cellulose gum solutions (1% w/w) were prepared by dispersing the gum in hot water which was allowed to gel overnight at 5°C. 50:50 (w/w) blends of each non-ionic gum solution with sodium carboxymethylcel-

TABLE 1

CELLULOSE GUMS INVESTIGATED

Generic name	Trade name	Supplier
Sodiumcarboxymethylcellulose (NaCMC)	Blanose 7HC	Hercules Powder Company, London
Hydroxypropylcellulose (HPC)	Klucel HF	
Xanthan gum	Xanthan gum A100	
Xanthan gum	Keltrol	ABM Chemicals, Stockport
Methylcellulose (MC)	Methocel A	Colorcon, Orpington Kent
Hydroxypropylmethylcellulose (HPMC)	Methocel E	
Hydroxypropylmethylcellulose (HPMC)	Metolose	Shin-Etsu Chemicals, Tokyo
Hydroxyethylcellulose (HEC)	Cellosize QP 4400H	Union Carbide, London
Methylhydroxyethylcellulose (MHEC)	Tylose MH50	Fabwerke-Hoechst AG Frankfurt

lulose solution (1% w/w) were prepared and mixed by inversion.

(2) Rheology. Assessment of the rheological properties of the cellulose solutions were carried out at room temperature (22°C) using a Haake Rotovisko (Haake, Berlin, F.R.G.) fitted with either a MK50 or MK500 spring and MVII cup and bob. The solution was introduced into the cup and allowed to equilibrate for 10 min. The shear stress at 10 different shear rates (2.72–441.0 s^{-1}) was then obtained.

(3) Interpretation. The shear stress–shear rate results were interpreted graphically using the following equations (Kabre et al., 1964):

$$F^N = \eta G \tag{1}$$

where F = shear stress (Nm^{-2}); G = shear rate (s^{-1}); N = material constant; η = viscosity coefficient.
By taking logs:

$$\log G = N \log F + \log \frac{1}{\eta} \tag{2}$$

A log–log plot of shear rate vs shear stress will be linear for pseudoplastic materials with a gradient > 1. The apparent viscosity ($\eta_{app} \cdot cP$) at each shear rate was calculated using the following equation:

$$\text{apparent viscosity } (\eta_{app}) = \frac{\text{shear stress (F)}}{\text{shear rate (G)}} \times 100 \text{ cP} \tag{3}$$

The mean calculated viscosity ($\bar{\eta}_i$) of the blends were calculated at each shear rate, i, using the following equation:

$$\log \bar{\eta}_i = x_A \log \eta_i^A + x_B \log \eta_i^B \tag{4}$$

where η_i^A = experimental (apparent) viscosity of 1% solution of component A at shear rate i; η_i^B = experimental (apparent) viscosity of 1% solution of component B at shear rate i; and x_A, x_B are the weight fractions of component A and B, respectively. The % change in viscosity was calculated from:

$$\frac{[\text{apparent viscosity } (\eta_{app}) - \text{calculated mean viscosity } (\bar{\eta})] \times 100}{\text{calculated mean viscosity } (\bar{\eta})} \tag{5}$$

Results and discussion

Chemical structure

Cellulose has a structure consisting of interlinked D-glucose units with each residue having 3 uncombined hydroxyl groups. Each unit is β-1,4-linked and at right angles to its neighbour (Fig. 1).

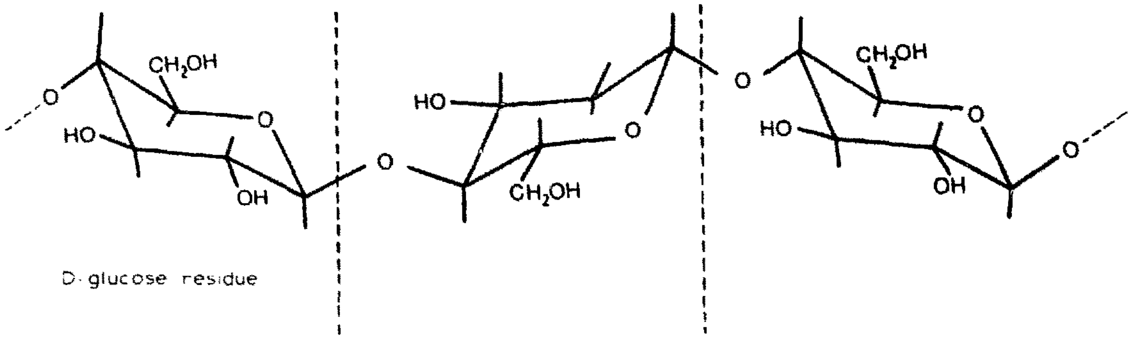


Fig. 1. Cellulose structure.

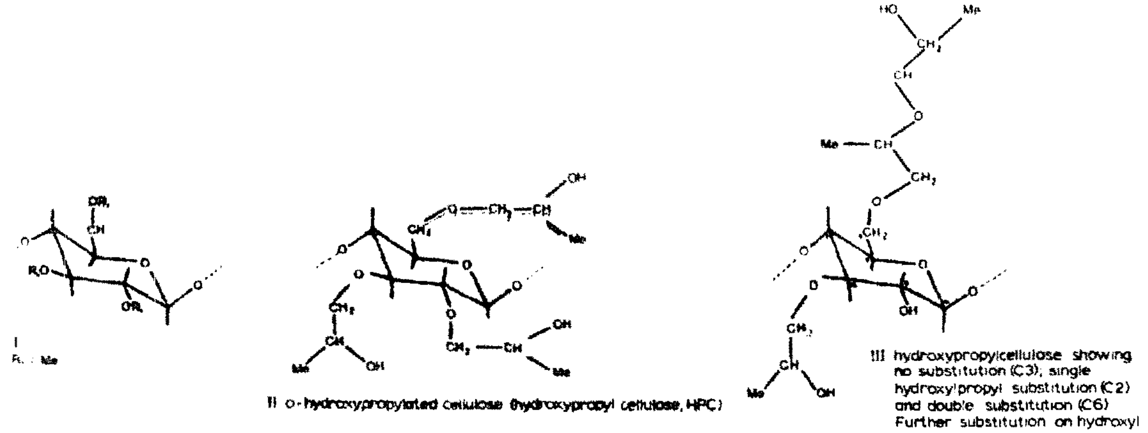
These long polymer chains are cross-linked by hydrogen bonds between hydroxyl groups on the glucose residues.

Cellulose gums are derivatives of cellulose that have the hydroxyl groups partially alkylated (Fig. 2I) or hydroxylalkylated (Fig. 2II) to give alkyl chains on the cellulose structure. In the latter case the hydroxyl groups on the alkyl chain can also be further hydroxyalkylated (Fig. 2III).

Thus a wide range of cellulose gums can be prepared with different types and degree of substitution. The average number of glucosidic hydroxyl groups substituted is termed the 'degree of substitution' (DS) and will play an important part in determining cross-linking capabilities.

Cross-linking and molecular interpretation

Cellulose gums act as thickeners of aqueous solution because of the dissolution, hydration and subsequent uncoiling of the polymer chains to form an entangled structure with some cross-linking. The flow of the continuous aqueous phase is then impeded when the solution is sheared and greater shearing rates cause the chains to become more linearly orientated and the apparent viscosity decreases. Accordingly



I
R = Me

II o-hydroxypropylated cellulose (hydroxypropyl cellulose, HPC)

III hydroxypropylcellulose showing no substitution (C3); single hydroxypropyl substitution (C2) and double substitution (C6) Further substitution on hydroxyl groups can occur

Fig. 2. Cellulose gum structures showing *o*-hydroxyalkyl substitution.

all the cellulose solutions studied were pseudoplastic (shear rate thinning) and linear plots were obtained for log(shear rate) against log(shear stress) according to Eqn. 2.

Cellulose gums can cross-link between the glucose residues and also between their alkyl chains and such interactions can occur when non-ionic gums (for example, hydroxypropylmethyl cellulose) and ionic celluloses (for example, sodium carboxymethylcellulose; NaCMC) are mixed together in solution. This cross-linking arises from hydrogen bonding (Rees, 1972; Allgen and Roswall, 1954) of the hydroxyl groups on the glucose residues in the same species (Fig. 3B) and with the carboxyl groups of the ionic NaCMC (Fig. 3A).

The addition of NaCMC to a non-ionic cellulose like hydroxypropylmethylcellulose (Methocel E4M) gives an average viscosity increase of 111% over the calculated viscosity using partial fractions (Fig. 4). Interestingly, other gums with similar viscosity specifications (e.g. Metolose 60SH-4000, 65SH-4000 and 90SH-4000) gave much smaller synergism (30–40%) while hydroxypropylcellulose (Klucel HF) methylhydroxyethylcellulose (Tylose MH 50) and methylcellulose (Methocel A4C) gave larger increases of 77, 186 and 230, respectively.

However, in some cases a smaller increase in the viscosity was obtained with HPMC. Methocels E5, E15 and E50 (Table 3) have comparatively low viscosities and correspondingly short chain-lengths. This drastically reduces the number of hydroxyl groups available for cross-linking with NaCMC and accordingly less synergism is obtained. The synergism is related to chain-length and viscosity. The dilution of a 1% NaCMC solution to 0.5% reduces the viscosity by as much as 82.4% depending on the shear rate. This will also explain the smaller synergism when in combination with low viscosity grades of HPMC.

In general then, it seems clear that the strength of cross-linking between non-ionic and ionic gums is greater than between molecules of the same species due to greater and stronger hydrogen bonding (Fig. 3). Hydrogen bonding between a carboxyl group (NaCMC) and a hydroxyl group (non-ionic gum) (Fig. 3A) should be stronger than between two hydroxyl groups (non-ionic gums) (Fig. 3B) of the same molecule.

The observed viscosity increases may be due to several other factors. Intermolecular hydrogen bonding between cellulose derivatives has also been explained in terms

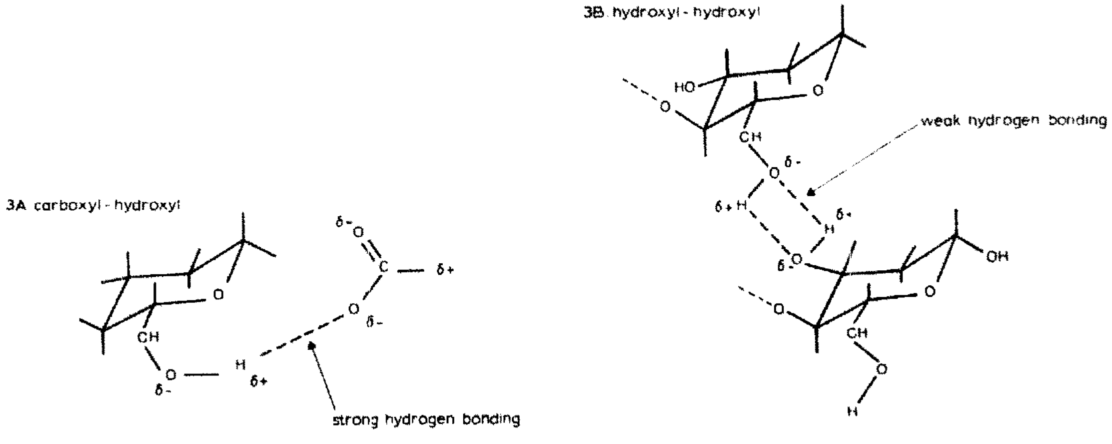


Fig. 3. Possible hydrogen bonding interactions of cellulose gums.

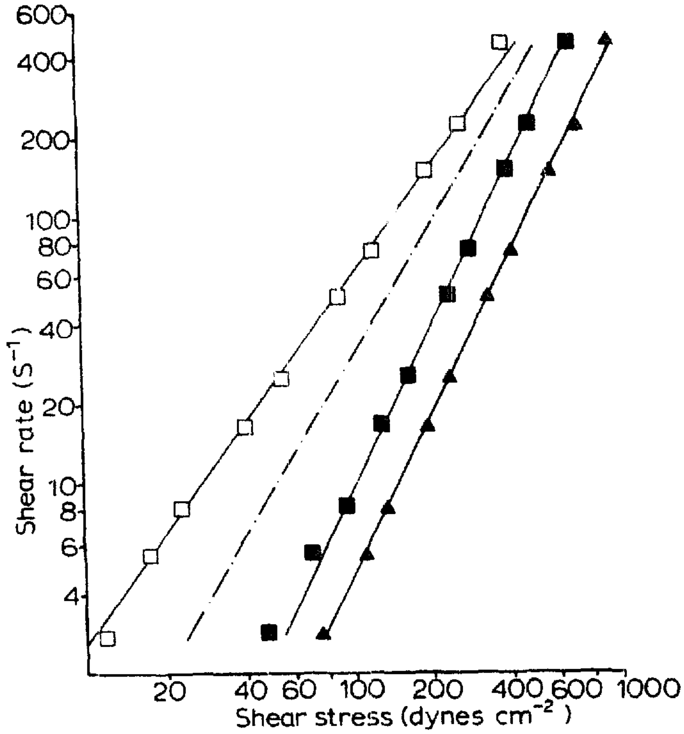


Fig. 4. Variation of shear rate and shear stress for HPMC, NaCMC and their 50:50 mixture. ■———■, 1% w/v NaCMC; □———□, 1% w/v HPMC (Methocel E4M); ▲———▲, 50:50 mixture (experimental); ·—·—·, 50:50 mixture (calculation).

TABLE 2

VISCOSITY CHANGES OF DIFFERENTLY SUBSTITUTED CELLULOSE GUMS WHEN MIXED WITH NaCMC

Cellulose substituent and trade name	Viscosity at 147 s^{-1} (cps)		Mean % viscosity increase 49–441 s^{-1}	Intercept at zero shear rate (%)
	1% soln	Mixture		
Methyl- (Methocel A4C)	28.7	276.8	230.6	281.5
Hydroxyethyl- (Cellosize QP4400H)	102.9	361.5	116.3	182.2
Methylhydroxyethyl- (Tylose MH50)	13.0	185.6	186.1	214.3
Hydroxypropyl- (Klucel HF)	147.2	358.3	77.1	126.7
Hydroxypropylmethyl- (Methocel E4M)	136.8	407.1	111.6	174.1
Xanthan gum				
Hercules	104.2	126.4	−33.8	−68.2
Keltrol F (ABM)	123.0	67.7	−59.1	−41.1

TABLE 3

VISCOSITY CHANGES OF HYDROXYPROPYLMETHYLCELLULOSE: SODIUM CARBOXYMETHYLCELLULOSE MIXTURES

Non-ionic cellulose	Viscosity at 147 s^{-1} (cP)		Mean % viscosity increase 49–441 s^{-1}	Intercept at zero shear rate (%)
	1% soln.	Mixture		
Metolose				
90SH-100	15.6	123.8	103.4	122.1
65SH-400	30.0	146.6	90.7	120.2
65SH-1500	66.4	182.3	56.9	66.5
60SH-4000	149.8	263.8	40.4	38.7
65SH-4000	127.0	221.5	36.4	47.8
90SH-4000	146.6	241.0	34.3	42.5
90SH-15,000	335.5	351.7	30.1	43.7
90SH-30,000	397.3	390.8	31.6	44.1
Methocel				
E5	9.1	79.5	45.6	22.1
E15	10.4	88.6	50.8	17.1
E50	11.7	109.4	66.6	46.6
E4M (4000)	136.6	407.1	111.6	174.1
E15M (15000)	302.9	432.4	43.3	66.4

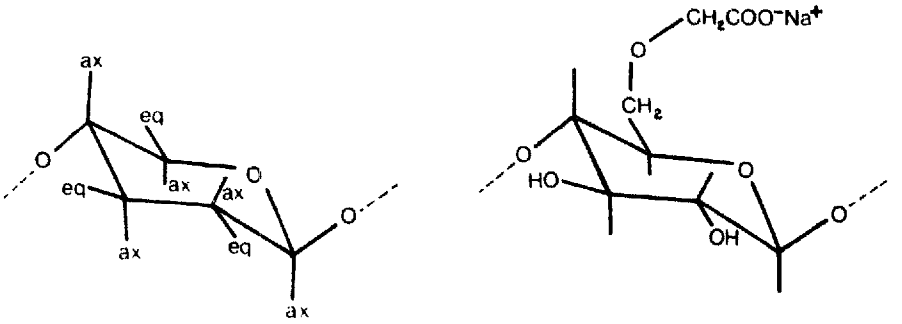
of the number of equatorial hydroxyl groups on the sugar residues (Levy, 1961). The equatorial positions (eq) are less crowded sterically and therefore more accessible to cross-linking than the axial positions (ax). Intermolecular hydrogen bonding would be greater between carboxymethyl and hydroxyalkylcellulose than between alginates for example. Equatorial and axial positions are shown in Fig. 5.

For all the gums studied, however, the different extents of viscosity increase cannot be explained in this way since all the unsubstituted hydroxyl groups are in equatorial positions.

However, accessibility of the hydroxyl group(s) on the alkyl chain substituents may contribute to the synergism. A longer side-chain will have a more exposed hydroxyl group at the terminal end which can then undergo interactions more easily with the carboxyl groups of NaCMC. If this is the case, hydrogen bonding would be greater in the series, HPMC > HPC > HEC > HMC. Nevertheless for the range of alkylcelluloses studied (Table 2) it is difficult to equate the viscosity increase with the type of substituent since other factors, notably degree of substitution, cellulose chain-length and viscosity grade will also contribute to the synergism observed. However, when celluloses of approximately equal viscosity are compared for example, HEC, HPC and HPMC; Table 2, a trend does emerge.

The degree of synergism seems most related to the substituent homologous series since synergism is in the order: MC > MHEC > HEC > HPMC > HPC (Table 2).

Rees (1972) proposed the formation of micellar structures when hydroxyalkyl



Cellulose

NaCMC showing unsubstituted-OH groups in equatorial positions

Fig. 5. Cellulose structures showing axial and equatorial positions.

cellulose gums are in solution. The micellar cross-links do not depend on a cumulative effect of weak interactions which would require an intimate fit of the chain together. The sugar residues cluster together haphazardly with cross-linking, and therefore synergism can occur easily by hydrogen bonding. Although chains may be in random motion they still form micellar structures. Other gums behave differently. For example, with l-carrageenan and furcellaran, a close fit of respective helical structures is required for chain cross-linking (Rees, 1972), and alginate gels cross-link by 'stacking' mechanisms with metal ions (e.g. Ca^{2+}) dispersed between parallel sugar residue layers. However, in the case of cellulose gums where the chains are randomly orientated there is no need for a regular covalent structure and hydroxyalkyl cellulose chains can cross-link even though the sugar residues may be irregular in shape.

Fundamentally, Rees (1972) suggested that the number and arrangement of these cross-links depends on the degree of substitution of each glucose residue which determines the balance of hydrophobic and hydrophilic groups on the residue chain. Hydrophobic zones are classified as those where substitution is heavy and similarly hydrophilic areas are where substitution is small or non-existent. Accordingly if the degree of substitution is low, water solubility will be greater than for more highly substituted celluloses. Indeed, ethylcellulose is generally water-insoluble. However, water-soluble grades are available that have a low degree of substitution.

Cross-linking of heavily substituted hydrophobic areas was thought to occur to a greater degree because of the associated lower smaller water solubilities of these portions of the sugar residues (Rees, 1972). Thus they tend to cluster together in an irregular way leaving relatively hydrophilic areas exposed to solvent, and also joining each chain cluster together in the form of a weak interlocking structure. This behaviour is analogous to surfactant micelles. Higher substitution (a higher DS value) will give greater cross-linking and a higher synergistic increase. This is observed in part for Metolose and Methocel (hydroxypropylmethylcelluloses) with similar chain-lengths (or molecular weights), and thus viscosity specification. If the lower viscosity of Metolose 65SH-4000 is taken into account then the synergism observed increases with the DS value. This is shown in Table 4.

The viscosity increase is in the same order as the methoxy content for the

Metolose cellulose but the viscosity increase for Methocel E4M cannot be compared to its methoxy content. In this case other factors must be more important in determining the extent of cross-linking. For example, the longer chain alkyl group may influence the cross-linking more.

In solution or where the cellulose chains clump together in a random way it is unlikely, however, that one hydroxyl group may be more accessible to cross-linking than another and this would explain why chemical content (i.e. % methoxy- or hydroxypropoxy-) cannot be correlated with the viscosity change.

In any case a more important factor is likely to be the viscosity grade (or chain-length/molecular weight of the cellulose).

The viscosity changes for the hydroxypropylmethylcelluloses studied are shown in Table 2. The Metolose celluloses exhibited a maximum synergism at a nominal viscosity of 100 cP (2% aqueous solution). Above this, there was a rapid decrease in the amount of viscosity synergism (Fig. 6). Different behaviour was observed for the Methocel range with a maximum viscosity increase occurring when the nominal 2% viscosity was 3000 cP (1% aqueous solution = 140 cP) (Fig. 6). However, this maximum is followed by a sharp fall. A comparison of Methocel E4M (4000 cP) with E15M (15,000 cP) shows that the large viscosity difference between the grades is annulled by the proportionally greater increase with E4M when mixed 50:50 with NaCMC. This does not occur with Metolose 90SH 15,000 and 30,000.

The maxima may be explained by the following. At a specific cellulose chain-length, which corresponds to a particular viscosity grade, all the hydroxy groups of the non-ionic and carboxyl groups of NaCMC which are available for cross-linking by micellar interactions have done so. This gives the observed synergistic viscosity increase. Any further lengthening of the non-ionic cellulose chain, i.e. an increase in the number of available hydroxyl groups will not produce a greater viscosity increase since there are no more available carboxyl groups. Therefore although the initial viscosity of the longer chain polymer is higher, the apparent increase in viscosity is smaller, even though there may be self-cross-linking of the cellulose chain.

TABLE 4

% VISCOSITY INCREASES RELATED TO THE CHEMICAL STRUCTURE OF HPMC AT THE SAME VISCOSITIES

Cellulose	Quoted viscosity (2%, 20°C) (cP)	Viscosity of 1% soln. at 147 s^{-1}	Chemical content		Degree of substn. (DS)	Mean % increase over calc. value
			-OMe	-OPrOH		
Metolose						
60SH-4000	3500-5600	149.8	29.0	9.5	1.88	40.4
65SH-4000	3500-5600	127.0	28.0	5.75	1.76	36.4
90SH-4000	3500-5600	146.6	21.5	8.0	1.39	34.4
Methocel						
E4M	4000	136.8	29.0	8.5	1.9	111.6

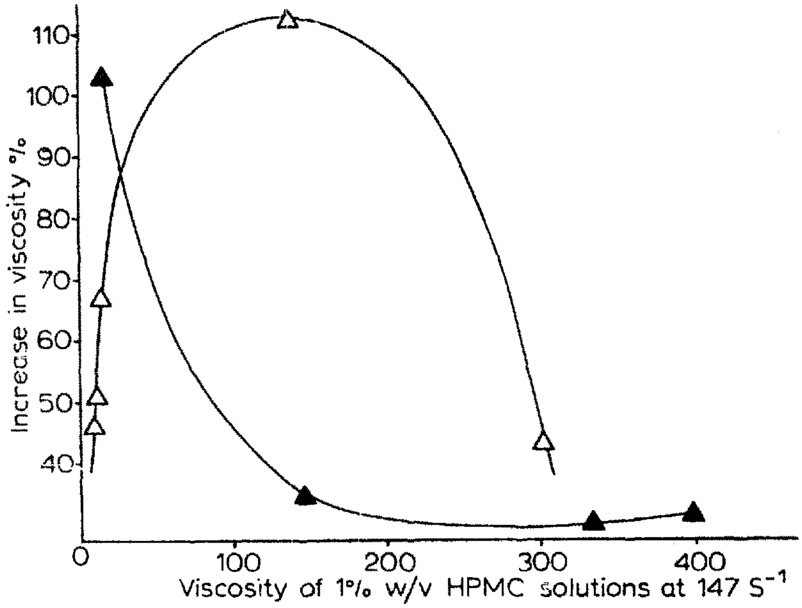


Fig. 6. Viscosity synergism between NaCMC and different viscosity grades of HPMC △——△, Methocel celluloses (HPMC); ▲——▲, Metolose celluloses (HPMC).

The % increase in viscosity is relatively constant over the measured shear range (49–441 s^{-1}) although considerable variation does occur at lower shear rates. The effect of variation in shear rate on the viscosity increase is shown in Figs. 7 and 8 for the hydroxypropylmethylcelluloses studied. Although there is a small decrease in the

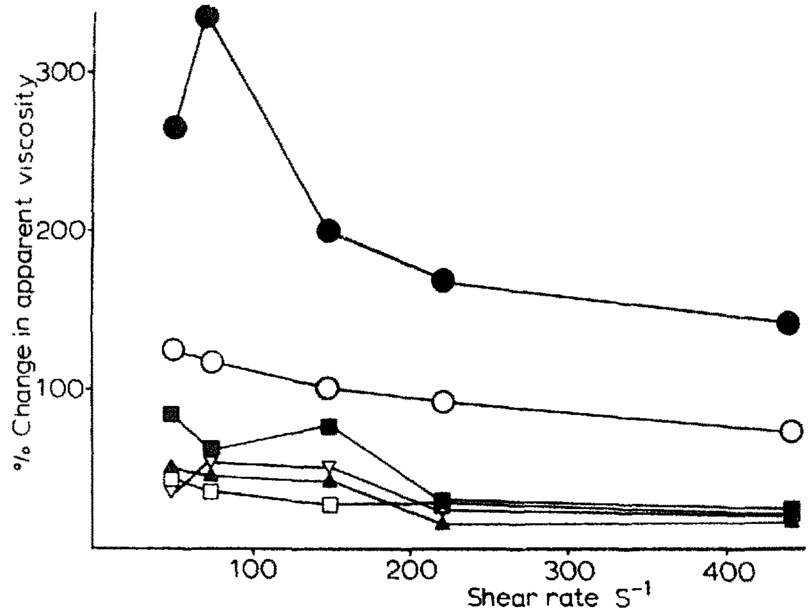


Fig. 7. Effect of shear rate on the apparent viscosity change of NaCMC and various grades of Methocel mixtures (50 : 50, 1% w/v). ▲——▲, Methocel E5; ▽——▽, Methocel E15; ■——■, Methocel E50; ○——○, Methocel E4M; □——□, Methocel E15M; ●——●, Methocel A4C.

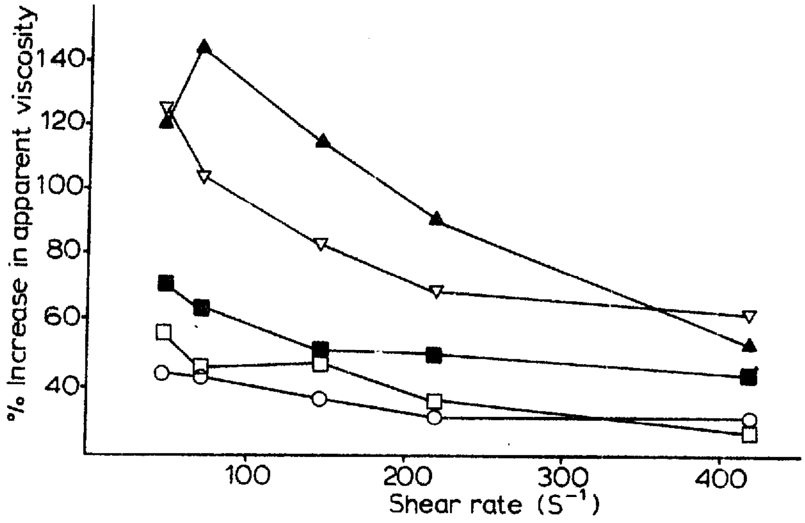


Fig. 8. Effect of shear rate on the apparent viscosity increase of NaCMC and various grades of Metolose celluloses (HPMC) mixtures (50:50, 1% w/v). ▲———▲, Metolose 90SH 100; ▽———▽, Metolose 65SH 400; ■———■, Metolose 65SH 1500; □———□, Metolose 65SH 4000; ○———○, Metolose 65SH 4000.

viscosity change as the shear rate increases in some instances, which will be caused by the disruption of any cross-linked structure by greater shear rates, there is no significant trend and overall the synergism is constant between 49 and 441 s^{-1}. It is

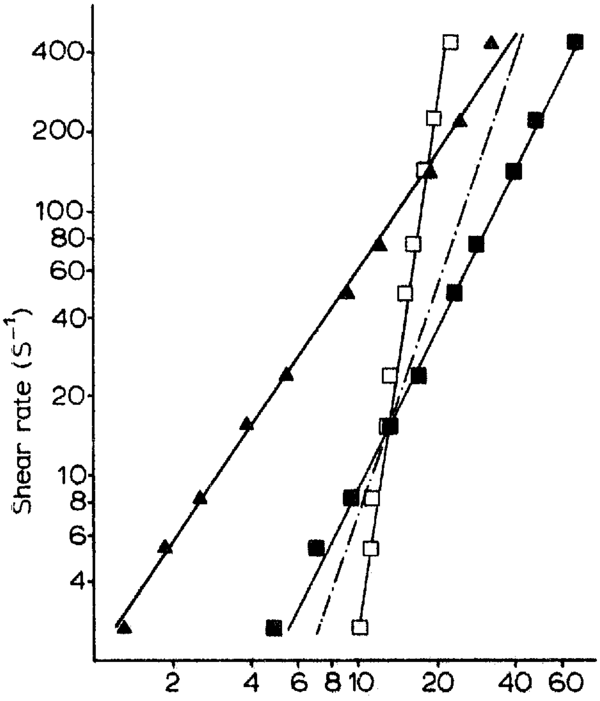


Fig. 9. Variation of shear rate and shear stress for xanthan gum, NaCMC and their 50:50 mixture. ■———■, 1% w/v NaCMC; □———□, 1% w/v xanthan gum; ▲———▲, 50:50 mixture (experimental); ·—·—·, 50:50 mixture (calculation).

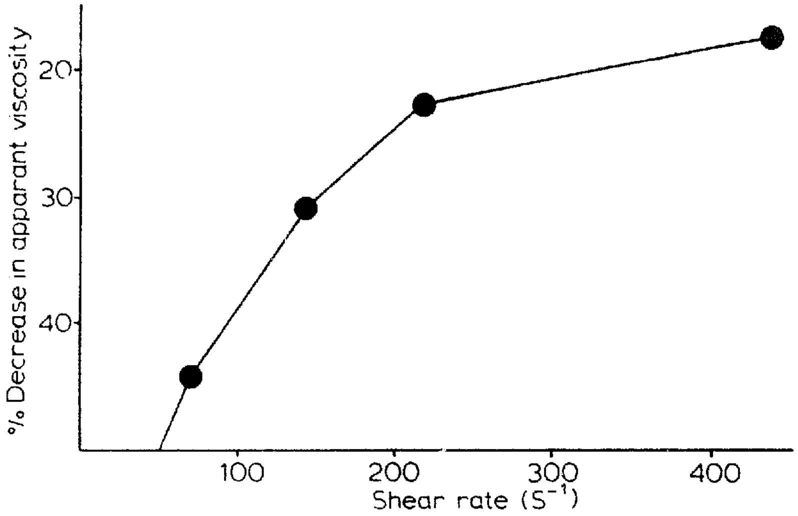


Fig 10. Effect of shear rate on the viscosity of xanthan gum : NaCMC (1% w/v aa).

also noticeable that very little change in the viscosity increase occurs for Metolose cellulose with a nominal viscosity of greater than 4000 cP. All the Metoloses above this value showed a 40–50% increase in viscosity over the 49–441 s^{-1} range.

NaCMC and xanthan gum are chemically incompatible due to the presence of the enzyme, cellulase, in the xanthan gum, which is difficult to completely remove during manufacture. This would break down the NaCMC structure and cause an apparent viscosity decrease.

The effect of shear rate on the viscosity change of xanthan gum (Hercules):NaCMC mixtures is shown in Fig. 10. At high shear rates, when the cellulose chains are linearly orientated, the effect of chain shortening, due to cellulose enzyme activity, is not so apparent as at lower shear rates where the shortened chains are probably coiled in micellar structures. Thus there is a lessening of the viscosity decrease at higher shear rates. Paradoxically this shear rate effect does not occur for mixtures of Keltrol (ABM Chemicals-xanthan gum) and NaCMC. Indeed the viscosity decrease observed is greater at higher shear rates. This cannot be explained.

Conclusions

By blending non-ionic cellulose gums with an ionic gum, sodium carboxymethylcellulose, a synergistic increase in viscosity is obtained. The calculation of mean viscosities by partial fractions assumes that no interaction occurs between the non-ionic and ionic cellulose whereas an increase indicates some degree of interaction. This increase in viscosity over the calculated value is due to stronger cross-linking between the two gums, where the presence of carboxyl groups on the NaCMC promotes stronger hydrogen bonding. In solution, a non-ionic cellulose molecule may either cross-link with a NaCMC molecule, or with a molecule of the same structure. If this cross-linking occurs via the carboxyl group on NaCMC, and a greater extent of hydrogen bonding results, then a synergistic viscosity increase is obtained.

It is difficult to correlate the viscosity increase with any known properties of the non-ionic celluloses but it seems probable that several contributory factors are important.

(1) The degree of substitution and alkyl substituent content will be influential because they will alter the available number of hydroxyl groups for cross-linking. The degree of substitution of the cellulose will also affect the hydrophobicity of the cellulose chain, the resultant micellization of the cellulose molecules, and the viscosities of the mixtures.

(2) The nature of the substituent hydroxyalkyl group may change the accessibility of the hydroxyl group available for cross-linking. However, in view of the random micellization proposed by Rees (1972) for cellulose gums in aqueous solitions, this would seem less probable.

(3) The chain-length (and the viscosity grade) of the non-ionic cellulose will alter the number of hydroxyl groups available for cross-linking interactions with NaCMC. An increase in the chain-length will cause greater synergism until a point is reached where the non-ionic cellulose is maximally cross-linked with NaCMC. The number of such interactions is related chiefly to the concentration and chain length (= viscosity grade) of the ionic NaCMC and a larger number of available hydroxyl groups on the non-ionic cellulose chain will not increase the degree of cross-linking. Consequently, a greater than optimum chain-length of the non-ionic gum will cause a smaller viscosity increase because the longer-chained celluloses have a greater initial viscosity.

The blend of NaCMC with xanthan gum produces a reduction in the apparent viscosity of the mixture due to enzymic breakdown of NaCMC.

By blending NaCMC with a non-ionic gum, particularly HPMC, a synergistic viscosity increase occurs which consequently reduces the level of thickeners required in many formulations.

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