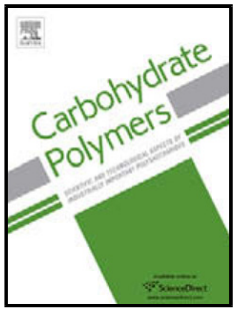
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Title	Effect of molecular weight on the ability of guar gum to enhance "weak gel" rheology of microdispersed oxidised cellulose (MDOC)
Authors	Xie, Xuehai;Agoub, Agoub A.;Morris, Edwin R.
Publication date	2017-04-21
Original Citation	Xie, X., Agoub, A. A. and Morris, E. R. (2017) 'Effect of molecular weight on the ability of guar gum to enhance "weak gel" rheology of microdispersed oxidised cellulose (MDOC)', Carbohydrate Polymers, 169, pp. 393-397. doi: 10.1016/j.carbpol.2017.04.039
Type of publication	Article (peer-reviewed)
Link to publisher's version	10.1016/j.carbpol.2017.04.039
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PII: S0144-8617(17)30428-9
DOI: http://dx.doi.org/doi:10.1016/j.carbpol.2017.04.039
Reference: CARP 12227

To appear in:

Received date: 14-3-2017
Accepted date: 18-4-2017

Please cite this article as: Xie, Xuehai., Agoub, Agoub A., & Morris, Edwin R., Effect of molecular weight on the ability of guar gum to enhance “weak gel” rheology of microdispersed oxidised cellulose MDOC.*Carbohydrate Polymers* http://dx.doi.org/10.1016/j.carbpol.2017.04.039

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Effect of molecular weight on the ability of guar gum to enhance "weak gel" rheology of microdispersed oxidised cellulose (MDOC)

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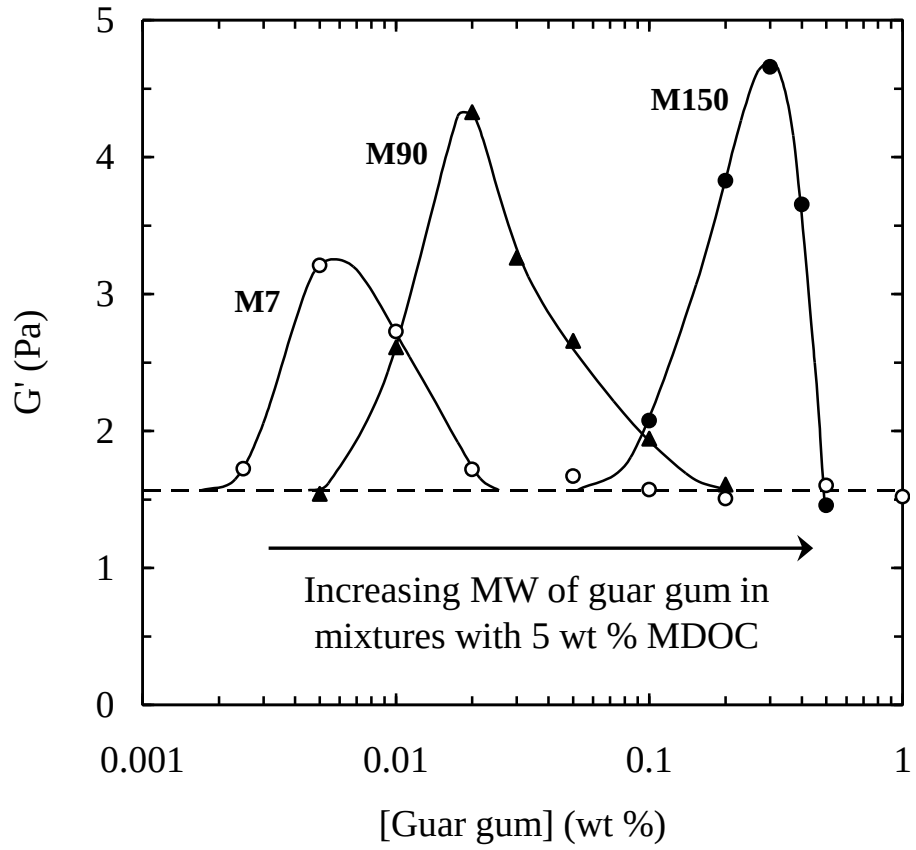
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Graphical Abstract



Highlights

- Self-association of MDOC promoted by segregative interactions with guar gum
- Causes initial increase in G' of "weak gels" formed by 5 % MDOC
- Decrease at higher concentrations due excessive aggregation of MDOC particles
- Concentration giving maximum G' increases with increasing molecular weight
- Larger coils have more internal segments that cannot make contact with MDOC

Abstract

MDOC comprises small, essentially insoluble, particles which associate to form "weak gel" networks at concentrations above ~4 wt %. Association is promoted by guar gum, causing an increase in G' at low levels of addition and a decrease at higher concentrations, due to excessive aggregation of the MDOC particles. For guar gum samples with molecular weights ranging from ~60 to ~1800 kDa, we found that the concentration required to give maximum G' for 5 wt % dispersions of MDOC increased systematically from ~0.005 wt % for the

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lowest molecular weight to ~0.3 wt % for the highest. We propose that guar gum drives self-association of MDOC to reduce enthalpically-unfavourable (segregative) interactions between the two materials, and that large coils are less effective than smaller ones because a higher proportion of chain sequences are buried in the interior of the coil, where they cannot make segmental contacts with the MDOC particles.

Keywords: Oxidised cellulose; MDOC; Oscillatory rheology; Segregative interactions; Thermodynamic incompatibility; "Weak gel"

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1. Introduction

Oxidised cellulose is produced using oxides of nitrogen, or other nitrogen-based oxidising agents, to replace the C(6) hydroxymethyl groups of glucose by carboxyl groups (Bertocchi, Konowicz, Signore, Zanetti, Flaibani & Paoletti, 1995; Kumar & Yang, 2002; Wei, Kumer & Banker, 1996). The material used in this investigation was a proprietary product in which ~75 % of the glucose residues are converted to glucuronate and solubility is restricted by Ca^{2+} cations, giving small particles that are essentially insoluble in water. This material is known as "microdispersed oxidised cellulose" (MDOC).

In a previous study by Agoub & Morris (2008) it was found that aqueous dispersions of MDOC, although pourable, gave gel-like mechanical spectra at concentrations far below those required for close-packing, indicating a "weak gel" structure (Ross-Murphy, 1984) formed by association (adhesion) of the MDOC particles. The critical concentration (c_o) for network formation (G' > G") was ~4.0 wt %; at values of concentration (c) well above c_o, G' showed the c^2-dependence commonly seen (Clark & Ross-Murphy, 1985) for gelling biopolymers.

In a recent investigation by Agoub, Xie, & Morris (2017) MDOC was used at a fixed concentration of 5 wt % (chosen as only slightly above c_o), and the effect of progressive incorporation of guar gum ($[\eta] \approx$ 12.1 dl/g; molecular weight $\approx 1.42 \times 10^6$) was studied, showing an initial increase and subsequent decrease in G' as the concentration of guar gum was raised. The initial increase was attributed to enhanced self-association of MDOC particles to reduce thermodynamically-unfavourable contacts (segregative interactions) with guar gum, and the subsequent decrease to excessive aggregation (reducing the number of effective crosslinks in the "weak gel" network).

The purpose of the present work was to explore the effect of the molecular weight of guar gum on its ability to promote self-association of MDOC. A preliminary account of the research was presented at the international conference "Gums and Stabilisers for the Food Industry 17", June 25-28, 2013, Wrexham, UK, and appears in the published proceedings of the meeting (Agoub, Morris & Xie, 2014).

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2. Materials and methods

The MDOC used in this investigation was the same as that studied by Agoub & Morris (2008) and Agoub et al. (2017). It was kindly donated by Alltracel Pharmaceuticals PLC, Sallynoggin, Co. Dublin, Ireland, with the following technical information. MDOC is prepared as a mixed calcium/sodium salt, with equal molar concentrations of calcium and sodium cations (i.e. 2 equivalents of Ca^{2+} for each equivalent of Na^{+}), and is supplied as a finely dispersed powder. Approximately 85 % of the particles have diameter below 30 μm, with ~40 % below 5 μm. These particles are insoluble in dilute mineral acid, and show little solubility in water. The carboxyl content of the sample studied (expressed as COOH, on a dry-weight basis) was ~18 %, which corresponds to ~75 % conversion of the glucose units of cellulose to glucuronate residues.

The guar gum samples were identical to those used in the investigation of mixtures with calcium pectinate reported by Giannouli, Richardson, & Morris (2004a): Meyprogat M7, M30, M60, M90 and M150 from Meyhall. The intrinsic viscosities of these materials (Giannouli et al., 2004a), and the values of molecular weight derived from them by the Mark-Houwink relationship reported by Picout & Ross-Murphy (2002), are listed in Table 1.

Table 1. Intrinsic viscosity ([η]) and molecular weight (relative molecular mass, M_r) of guar gum samples

Sample	M7	M30	M60	M90	M150
[η] (dl g^{-1})	1.30	3.85	6.11	9.55	14.25
M_r (kDa)	60	280	538	1013	1786

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Dispersions of MDOC in distilled deionised water were prepared at a fixed concentration of 10 wt % by overhead stirring for 20 min at ambient temperature. Solutions of guar gum, also in distilled deionised water, were prepared at twice the required final concentrations, and were mixed with an equal weight of the MDOC dispersion, giving an MDOC concentration of 5 wt % in all samples (as in the investigation by Agoub et al. (2017)). The mixtures were then stirred for 30 min, using a magnetic stirrer.

Low-amplitude oscillatory measurements of storage modulus (G'), loss modulus (G") and complex dynamic viscosity (η^*) were made using highly truncated cone-and-plate geometry (50 mm diameter; 0.05 rad cone angle; 0.5 mm gap) on a sensitive prototype rheometer designed and constructed by Dr. R.K. Richardson, Cranfield University, UK. Temperature (controlled by a Haake circulating water bath) was held fixed at 20°C.
After loading, samples were coated around their periphery with light silicone oil, to minimise evaporation, and changes in G' and G" at 1 rad s^{-1} and 1 % strain were monitored over a period of 2 h. A mechanical spectrum (frequency-dependence of G', G" and η^*) was then recorded (at 1 % strain).

3. Results

The changes in G' and G" observed during the holding period of 2 h at 20°C for 5 wt % MDOC with no added guar gum are shown in Fig. 1a. There is a progressive increase in G' over time, with a much smaller accompanying increase in G", and G' is higher than G" throughout. The mechanical spectrum (Fig. 1b) recorded at the end of the holding period has obvious gel-like character. G' shows little dependence on frequency, and at low frequencies is more than 10 times higher than G". There is, however, a pronounced up-turn in G" at high frequency, indicating a significant "sol fraction" of material that does not form part of the "weak gel" network.

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The effect of guar gum on development of network structure by 5 wt % MDOC is shown in Fig. 2a, using Meyprogat M30 as an illustrative example. Incorporation of a very low concentration of M30 (0.005 wt %) caused a significant (~2-fold) increase in G' above the values observed in the absence of guar gum. Increasing the concentration to 0.01 wt % caused a further approximate doubling of G'. At 0.02 wt % M30, however, the observed values of G' throughout the 2 h holding period were substantially lower than at 0.01 wt %, and on further increase in the concentration of M30 to 0.05 wt % they became similar to those observed for 5 wt % MDOC with no added guar gum.

Reduction in moduli on increasing M30 concentration from 0.01 to 0.05 wt % is also shown by the mechanical spectra (Fig. 2b) recorded after 2 h at 20°C. It should be noted, however, that the values of G' observed (Fig. 2a) at the start of the holding period were substantially higher for the mixture of 5 wt % MDOC with 0.05 wt % M30 than for the same concentration of MDOC alone, which is consistent with the proposal (Agoub et al., 2017) that loss of network structure at guar gum concentrations above the optimum value is caused by excessive aggregation of MDOC particles.

As shown in Fig. 3, a similar initial increase and subsequent decrease in G' with increasing concentration of guar gum was observed for the other Meyprogat samples, but with gross differences in the concentration at which maximum enhancement occurred. This optimum concentration (c_{max}) became progressively higher as the molecular weight of the guar gum increased, ranging from ~0.005 wt % for M7 (Fig. 3a) to ~0.3 wt % for M150 (Fig. 3b).
As shown in Fig. 4, using M7 and M90 as illustrative examples, there is an initial reduction in tan δ (i.e. increasing solid-like character) as the concentration of guar gum (c) is raised towards c_{max} and a subsequent increase (loss of network cohesion) above c_{max}. Similar initial decrease and subsequent increase in tan δ as concentration was increased up to and beyond c_{max} was observed for the other guar gum samples.

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The values of G' and tan δ (1 rad s^{-1}; 1 % strain) plotted in Figs. 3 and 4 were taken from the mechanical spectra recorded after the samples had been held for 2 h at 20°C. It is evident from the traces shown in Figs. 1a and 2a, however, that the moduli had not reached stable values by the end of this holding period. Indeed, in the investigation by Agoub & Morris (2008) it was found that development of network structure by aqueous dispersions of MDOC (3.2 - 12.0 wt %) had not reached completion after holding for 15 h at 20°C, although the rate of increase in moduli became very slow at holding times greater than ~2 h (as used here).

Figure 5 shows a direct comparison between values of G' (Fig. 3) taken from the mechanical spectra and those recorded for the same samples at the end of the 2 h holding period. The moduli from the mechanical spectra are systematically higher, reflecting further self-association of MDOC during the time taken to record the spectra (~20 min), but the differences are comparatively small (~10 %), and essentially the same for all samples, suggesting that continued development of "weak gel" structure is unlikely to have caused any serious distortion of the mechanical spectra or of the curves shown in Figs. 3 and 4.

As shown in Fig. 6a, the maximum values of G' (G'_{max}) observed (Fig. 3) for mixtures of 5 wt % MDOC with each of the Meyprogat samples increases slightly as the intrinsic viscosity of the guar gum increases. This effect, however, is tiny in comparison with the massive accompanying increase in c_{max} (Fig. 6b), which shows clearly that the effectiveness of guar gum in promoting self-association of MDOC decreases steeply with increasing molecular weight (i.e. with small coils having a greater effect than larger ones). It should also be noted that, despite somewhat different experimental conditions, the value of $c_{max} \approx 0.042$ dl/g observed for the (Sigma) guar gum sample ($[\eta]$ = 12.1 dl/g) used in the study by Agoub et al. (2017) fits in smoothly with those observed for the Meyprogat series.

4. Discussion and conclusions

The main conclusion from the investigation by Agoub et al. (2017) was that very low concentrations of guar gum cause substantial enhancement in the strength of MDOC networks, but that gel strength decreases again at higher concentrations, due to excessive aggregation. The main conclusion from the present work is that the effectiveness of guar gum in promoting self-association of MDOC decreases as its molecular weight increases.

An inverse relationship between the molecular weight of guar gum and its ability to enhance the "weak gel" networks formed at high temperature (85°C) by low-methoxy pectin with stoichiometric Ca^{2+} was reported by Giannouli et al. (2004a). A similar inverse correlation has also been observed (N. McCarty, S.M. Fitzsimons & E.R. Morris, unpublished) between the molecular weight of guar gum and its ability

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to enhance thermogelation of whey protein isolate, by promoting self-association of denatured protein (Fitzsimons, Mulvihill, & Morris, 2008).

Decreased effectiveness with increasing molecular weight strongly indicates that enhanced gelation on incorporation of guar gum (or the other soluble polysaccharides studied by Giannouli, Richardson, & Morris (2004a,b,c)) does not arise from phase separation: increasing molecular weight decreases the number of polymer chains free to move independently and therefore decreases the entropic advantage of the polymers remaining in a single phase (entropy of mixing). It also argues against depletion flocculation (Dickinson, 1992), which arises from the inability of polymer coils to enter the gap between adjacent particles, and should again, therefore, become increasingly apparent as the size of the coils increases. It does, however, seem qualitatively consistent with a mechanism based on segregative interactions, as proposed by Agoub et al. (2017).

For disordered polymers of high molecular weight, a large proportion of the chain sequences will be buried in the interior of the polymer coil, where they cannot make segmental contacts with the other polymeric constituent in single-phase mixtures. As the molecular size decreases, however, the proportion of "wasted" interior sequences will also decrease, which could explain why small coils are more effective than larger ones.

Acknowledgements

We thank Dr. R.K. Richardson, Clophill, Bedfordshire, UK for generous access to his prototype rheometer and for repairs and maintenance of the instrument during the course of the investigation. We also thank Dr. Ivan Santar, Tisnov, Czech Republic for helpful discussions and Dr. Brona O'Neill, Alltracel, for kindly arranging supply of the MDOC sample studied. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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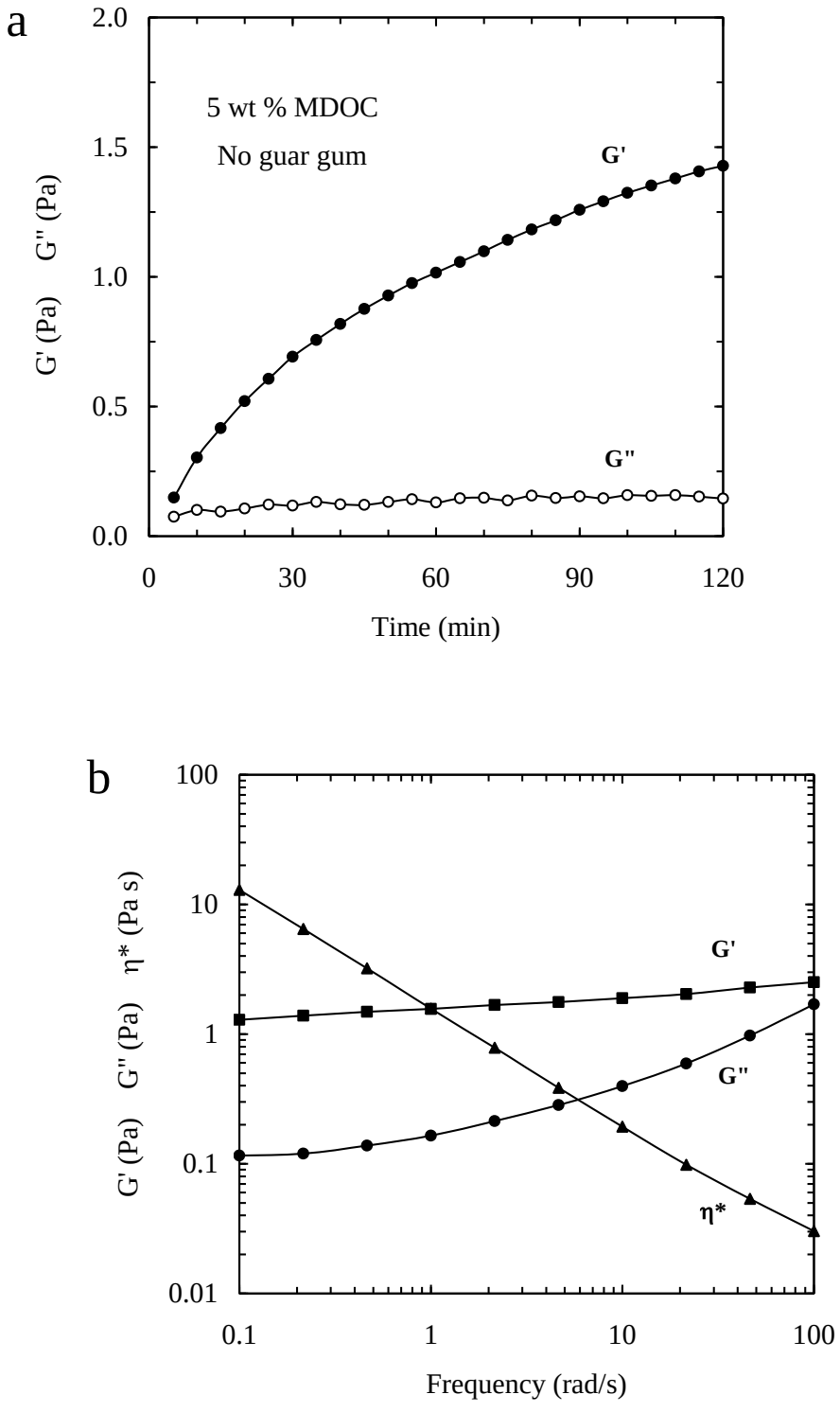


Fig. 1. (a) Changes in G' (●) and G" (○), measured at 1 rad s^{-1} and 1 % strain, for 5 wt % MDOC, with no added guar gum, on holding for 2 h at 20°C. (b) Mechanical spectrum (1 % strain) showing the frequency-dependence of G' (■), G" (●) and η* (▲) for the same sample after completion of the 2 h holding period.

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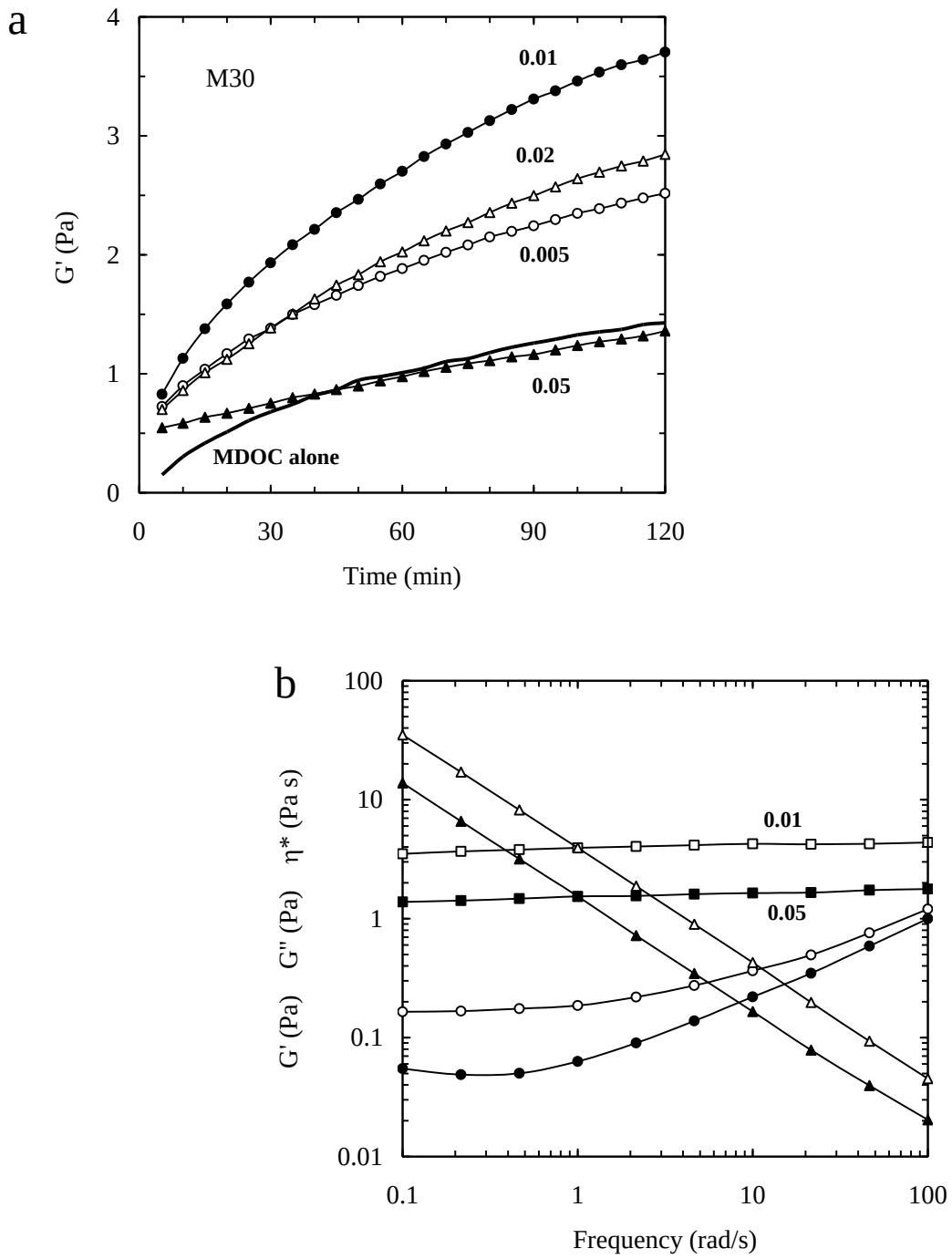


Fig.2. (a) Changes in G' (1 rad s^{-1}; 1 % strain) during holding for 2 h at 20°C for 5 wt % MDOC alone (——) and in mixtures with Meyprogat M30 guar gum at concentrations (wt %) of 0.005 (O), 0.01 (●), 0.02 (Δ) and 0.05 (▲). (b) Mechanical spectra (1 % strain) recorded after the 2 h holding period, showing the frequency-dependence of G' (squares), G'' (circles) and η* (triangles) for 5 wt % MDOC in mixtures with M30 at concentrations of 0.01 wt % (open symbols) and 0.05 wt % (filled symbols).

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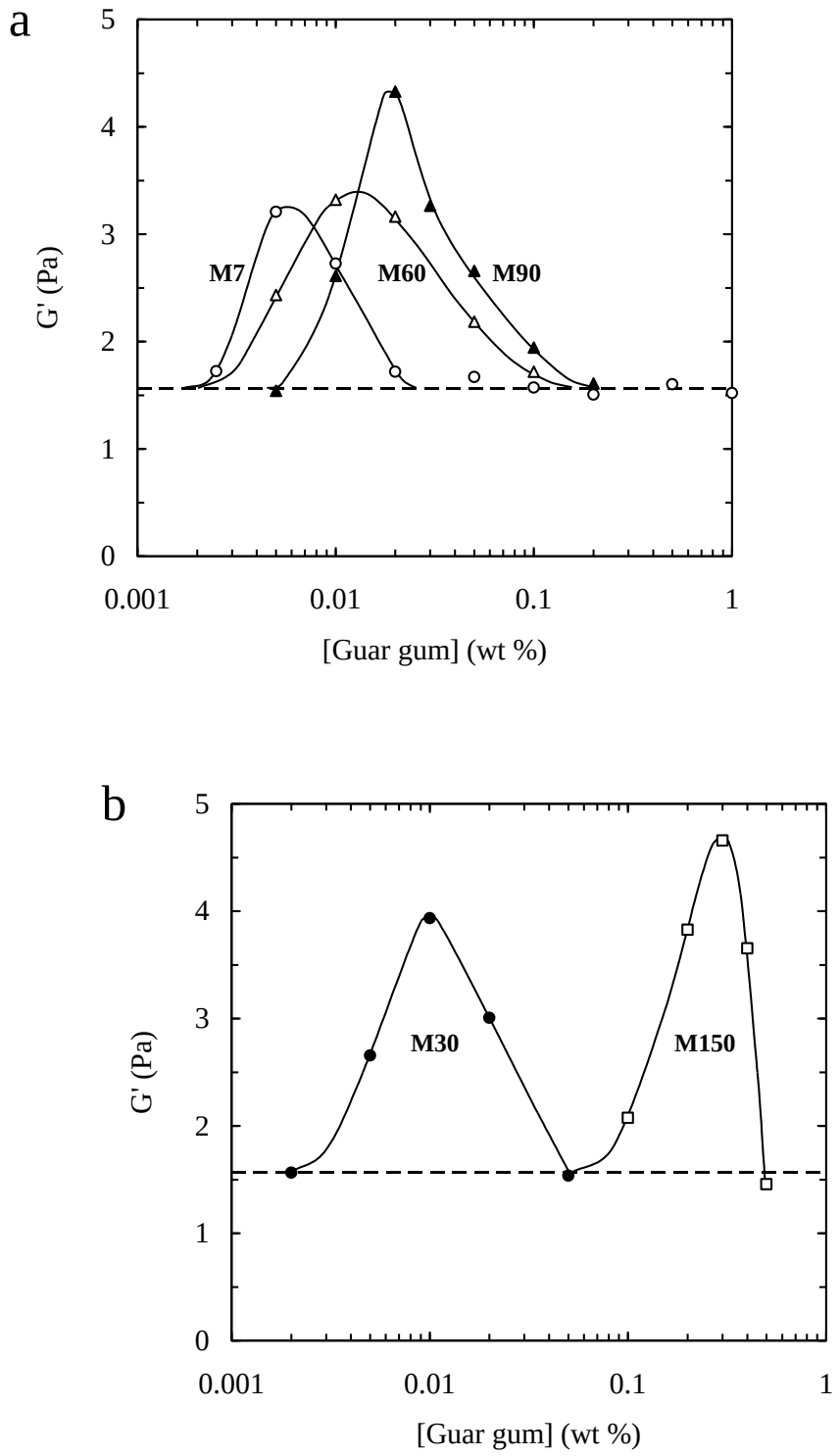


Fig. 3. Values of G' (1 rad s^{-1}; 1 % strain) taken from mechanical spectra recorded after 2 h holding at 20°C for 5.0 wt % MDOC alone (- - -) and in mixtures with guar gum samples M7

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(○), M30 (●), M60 (Δ), M90 (▲) and M150 (□). For clarity of presentation, results for M7, M60 and M90 are shown in frame (a), and those for M30 and M150 in frame (b).

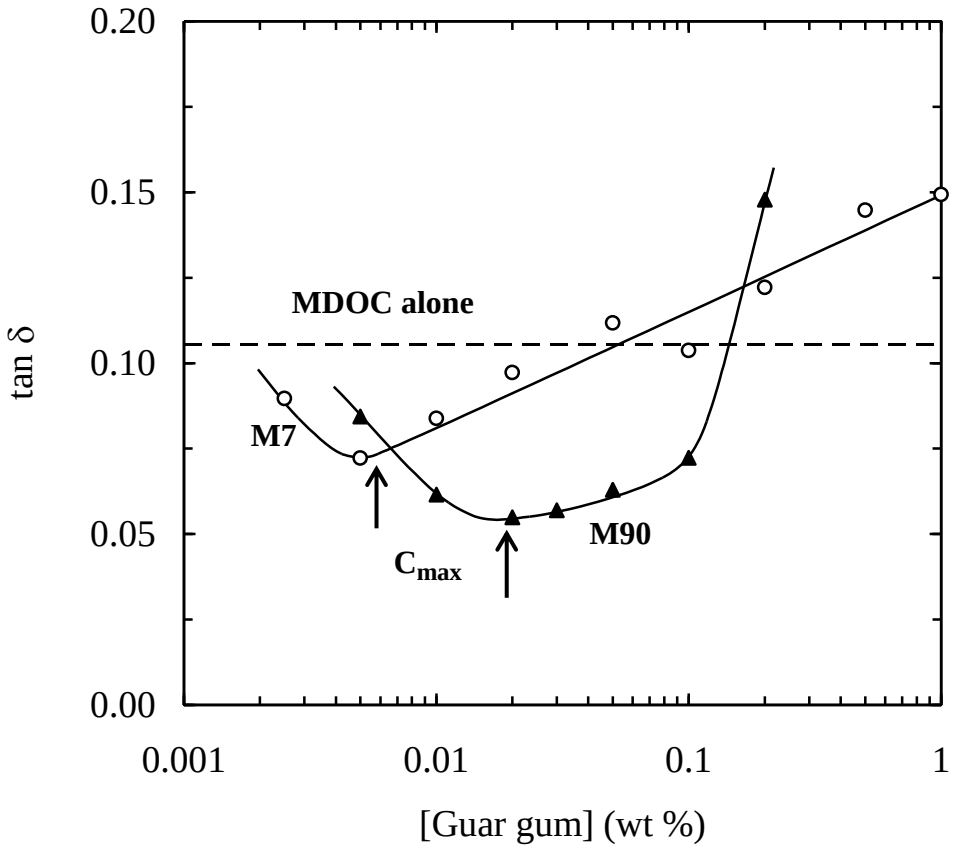


Fig. 4. Values of tan δ (1 rad s^{-1}; 1 % strain) taken from mechanical spectra recorded after 2 h holding at 20°C for 5.0 wt % MDOC alone (- - -) and in mixtures with guar gum samples M7 (○) and M90 (▲). The vertical arrows show the concentrations of guar gum (c_{max}) at which maximum enhancement in G' was observed (Fig. 3).

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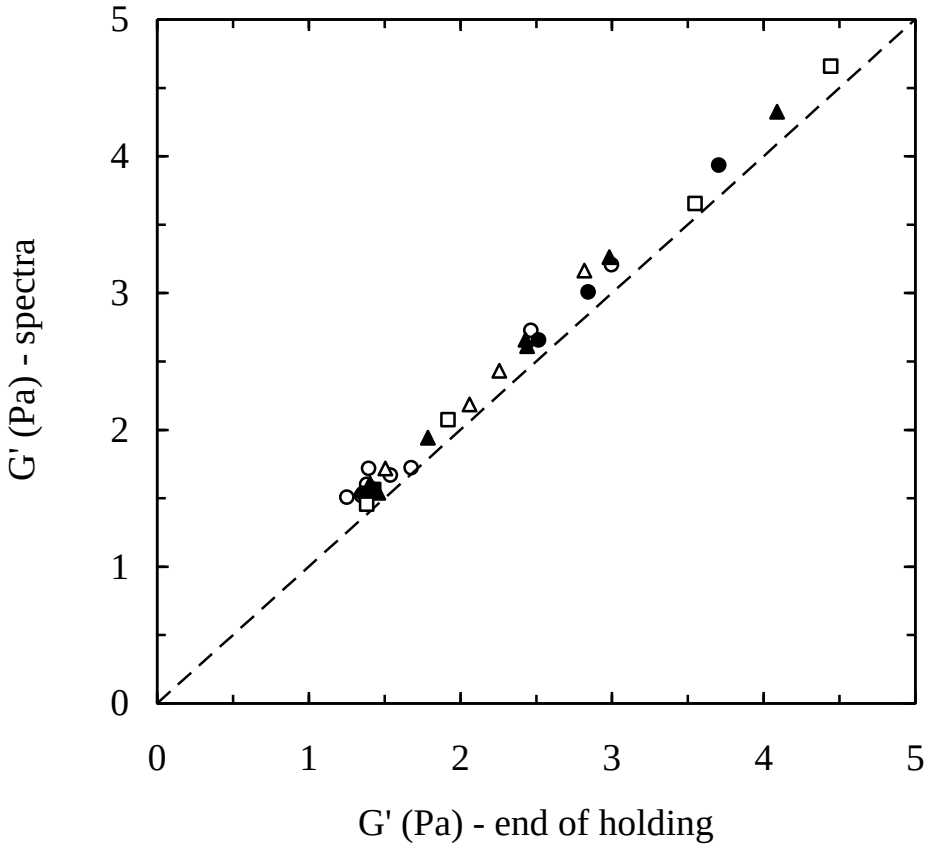


Fig. 5. Comparison of G' (1 rad s^{-1}; 1 % strain) on completion of holding for 2 h at 20°C (horizontal axis) and in mechanical spectra recorded immediately after the holding period (vertical axis) for 5.0 wt % MDOC in mixtures with guar gum samples M7 (○), M30 (●), M60 (Δ), M90 (▲) and M150 (□). The dashed line corresponds to identical values of G' at both times.

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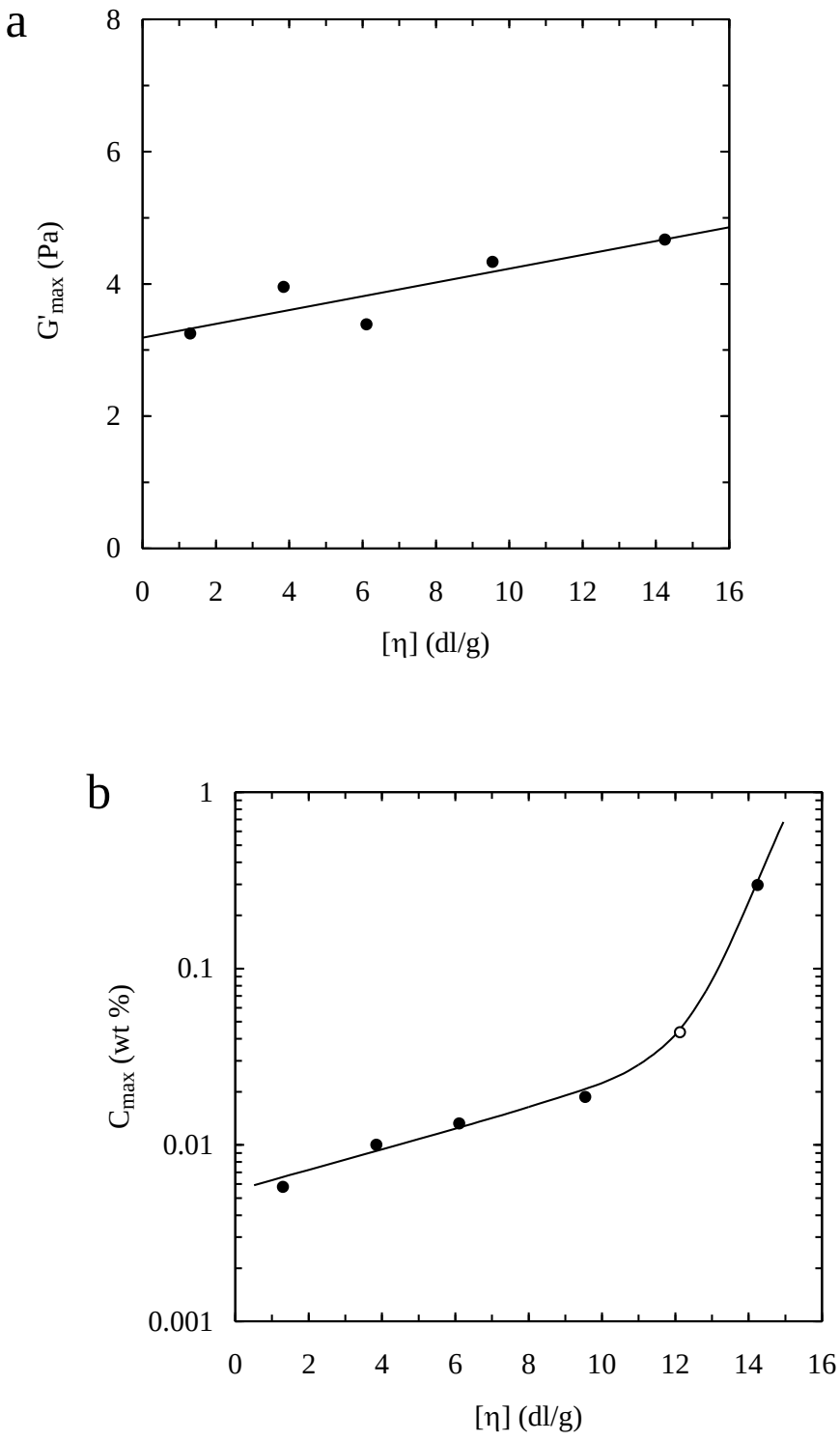


Fig. 6. Effect of intrinsic viscosity ([η]) of guar gum on (a) the maximum value of G' (G'_{max}) observed (Fig. 3) for mixtures with 5.0 wt % MDOC, and (b) the concentration of guar gum (c_{max}) at G'_{max}, for Meyprogat samples (●) and for the sample from Sigma (O) used in the investigation by Agoub et al. (2017).