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Thermogelling polysaccharides for aqueous gelcasting—part I: a comparative study of gelling additives

Arnaldo J. Millán[1], Rodrigo Moreno*, María Isabel Nieto

Instituto de Cerámica y Vidrio, CSIC, Crtra Valencia Km 24,300, 28500 Arganda del Rey, Madrid, Spain

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Abstract

In this work the rheological properties of aqueous solutions of three polysaccharides, agar, agarose, and carrageenan for aqueous gelcasting are studied. Solutions of these additives have been prepared to concentrations ranging from 1 to 4 wt.%. The dissolution and gelling behaviour are studied from the measurements of viscosity as a function of temperature on both heating and cooling. These additives need to be heated at >90 °C to dissolve, except carrageenan, where full dissolution is achieved at <70 °C. Dissolution temperature and Tg of carrageenan directly depend on concentration and do not change significantly for agaroids. The hystheresis of gelation is much broader for agaroids. The viscosity increases at least 1000 mPa.s on gelation when the concentration is $\geqslant 2$ wt.%. Gelation occurs for the three additives in a broad range of pH between 4 and 10. The gels are reversible but the temperature must be maintained above 50 °C to prevent gelation. The results show that carrageenan is a suitable candidate for gelcasting since its properties are near to those of agaroids and the cost is lower.

Keywords: Al_2O_3; Gelcasting; Gelling agents; Rheology

1. Introduction

The interest on colloidal processing of ceramics has grown in recent years as it provides improved microstructural design and reliability.[1–4] In colloidal processing a homogeneous and dense green body is formed from a stable suspension. Important relations between processing, structure and properties have been pointed out elsewhere. In a colloidal suspension the interparticle forces between the particles can be controlled and altered through careful control of the colloid chemistry.

Consolidation of dispersed particles into a compact body implies the removal of the suspending liquid by means of a filtration mechanism (as in the case of slip casting and pressure casting) or by evaporation (e.g. drying, in the case of tape casting and electrophoretic deposition, EPD). The first group is usually employed for manufacturing bulk complex shaped parts whereas tape casting is a suitable method for producing flat substrates and laminar structures. EPD is more versatile and allows us to obtain either shaped parts or substrates and coatings. Another family of colloidal shape forming routes is being developed in which the liquid is not removed and consolidation occurs when the starting suspension is forced to flocculate, coagulate or gelate.[5] Flocculation and coagulation lead to the formation of a network structure of the particles when electrostatic repulsion is minimised by shifting the pH toward the isoelectric point or by increasing the ionic strength (direct coagulation casting, clay-like forming) or by polymeric bridging when particles are dispersed with polymers.[6–8]

Gelation refers to the formation of a polymeric structure that retains the particles inside. Gelation can be induced chemically by polimerisation of monomers through a catalyst (i.e. gelcasting process) or thermally, where an aqueous suspension containing a gelling binder gelates on either heating (methylcellulose derivatives) or cooling (agaroids).

Much effort has been devoted recently to develop near-net shaping methods in water, because of the obvious health, safety and environmental benefits. This has increased the interest on searching for new gelling binders for aqueous media, the most effective being agar derivatives.

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* Corresponding author. Tel.: +34-9-1871-1800; fax: +34-9-1870-0550.

[1] Present address: Depto. Materiales, IUT Dr. Federico Rivero Palacios, Caracas. Venezuela.

E-mail address: rmoreno@icv.csic.es (R. Moreno).

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Agaroids were first described by Fanelli et al.[9] and further studied by several investigators.[10,11] They provide a high gel-strength to the green bodies when added in very low concentrations (typically around 1 wt.%). However, other polysaccharides have been also considered, such as gelatines,[12] starches,[13] gums,[14] etc. In previous studies we have proposed the family of carrageenans as high gel-strength binders with potential use in the manufacture of ceramic and metallic pieces.[15,16]

The effect of several thermogelling additives on the rheology of ceramic suspensions and their potential use in aqueous gelcasting or injection moulding of alumina has been previously studied, although we have also described the gelation of silicon nitride.[17,18]

To fully exploit the advantages of the gelling binder particular attention must be given to the way in which it is incorporated to the ceramic slurry. It has been demonstrated[19] that more homogeneous and denser materials may be obtained when the gelling binder is added to the ceramic suspension as a solution at 60–65 °C. However, this implies a reduction in the solid loading, thus affecting the viscosity, the mould filling, and the green properties. Hence, the concentration of the precursor solution and the total concentration of additive in the slurry have a key role in aqueous gelcasting.

The aim of this work is to study the rheological properties of aqueous solutions of three gelling binders (agar, agarose, and carrageenan) prepared at different concentrations as a function of the temperature. From the measurement of the evolution of viscosity on heating and cooling the temperatures of dissolution and gelation are determined, as well as the gelation hystheresis. The effect of binder concentration, pH, and shearing conditions on the viscosity has been studied as a function of temperature.

2. Background

Most gelling binders are polysaccharides constituted by chains of glycosyl units formed from hexoses and pentoses. The presence of oxygen atoms and hydroxil groups in those units make possible hydrogen bonding with water molecules.[20] This allows the total solvation of the chains and contributes to the water solubility.

When molecules of different chains bond together the acces to water is blocked and the resultant polysaccharide is not soluble. In this case crystalline arrangement occurs and a process of water exclusion (syneresis) is detected. Hence, a three-dimensional network with water molecules trapped troughout is obtained, thus giving a gel.

The family of agaroids has been succesfully employed in ceramic processing. Agar is a polygalactoside constituted by two major components: agarose and agaropectine. Agarose is the gelling fraction of agar and consists of repeating units (agarobiose) of alternating β-D-galactopyranosil and 3,6-anhydro-α-L-galactopyranosil groups.[21] Agaropectine has a similar structure but contains 5–10% sulphate esters and other residues. Fig. 1 shows the typical structures for agar and agarose, respectively.

Carrageenans are linear sulphonated polysaccharides with alternating 1,3-linked β-D-galactopyranosil and 1,4-linked α-D-galactopyranosil groups. There are several fractions, the most important from an industrial point of view being the so-called κ, ι, and λ fractions. The proportion of sulphates increases from 24.9% for a pure κ-carrageenan (minimum content) to a maximum of 52.2% for the λ-carrageenan. Their behaviour depends on the effect of different cations that can link to semi-ester sulphate groups. The gelling properties increase from λ to ι to κ, while viscosity decreases in that order. The maximum gel efficiency corresponds to a κ-carrageenan in the presence of K^+ ions at neutral or basic pH.[22] The structure of the κ-carrageenan is also shown in Fig. 1.

Gelation occurs on cooling below the glass-transition temperature, T_g, by hydrogen bonding that leads to the development of double helix structures. In the case of carrageenan with K^+ linked to the sulphate groups, an antiparallel double helix structure is formed. When the formed gel is reheated it does not dissolve but it melts, since polysaccharide molecules are already hydrated in the gel, so that the network breaks down into randomly coiled isolated chains. Both the melting and the dissolution temperatures coincide and remain constant for

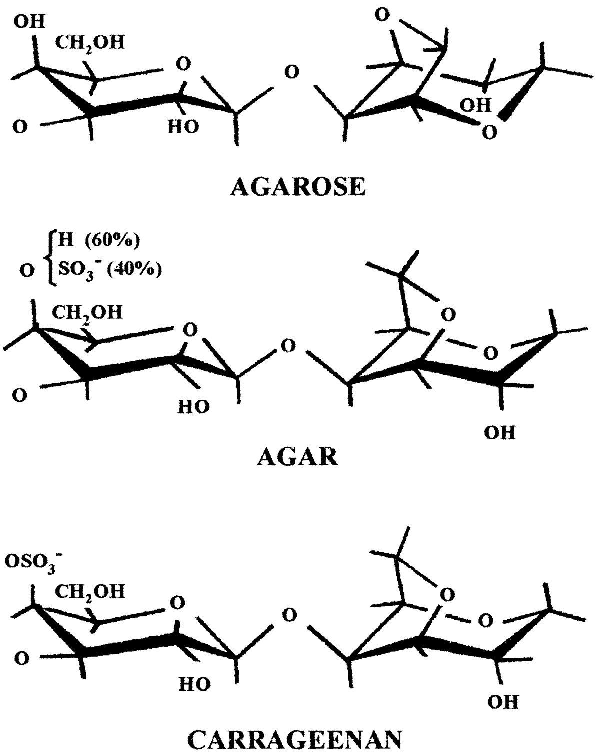

Fig. 1. Repeating unit of the three selected polysaccharides.

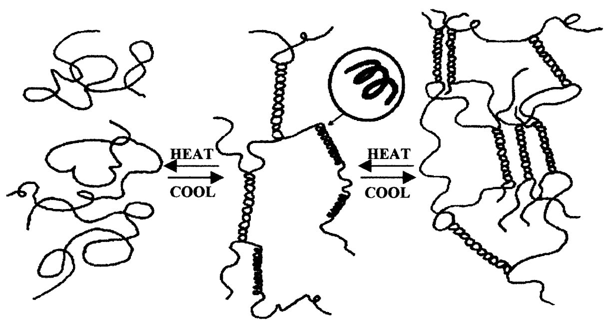

Fig. 2. Schematic representation of the double helix structure formed on cooling.

subsequent cooling/heating cycles. The gelation mechanism of these polysaccharides is schematically illustrated in Fig. 2.

3. Experimental

The studied gelling binders were: (1) agar (Grand Agar), (2) agarose (D1 LE), and (3) carrageenan (Secogel TC). They were all supplied by Hispanagar S.A. (Burgos, Spain) in the form of powders. The particle size distribution of these powders was measured using a laser diffraction analyser (Mastersizer S, malvern, UK). Dispersing media were water for agaroids and ethanol for carrageenan, since the last hydrates in water at room conditions. Fig. 3 shows that the mean particle size is ~100 μm for carrageenan and ~150 μm for agaroids.

Rheological behaviour was studied with a rheometer Haake, RS50 (Germany) under controlled rate conditions. A double cone geometry was used (DC60/2, Haake, with 60 mm in diameter and a cone angle of 2°). This measuring system has a covering plate that prevents evaporation and helps to maintain the temperature of the suspension.

For such measurements, the required quantity of binder powder was added to the water to concentrations of 1.5, 2, 3 and 4 wt.% and was then mechanically stirred at room temperature. These mixtures were introduced in the rheometer to perform the measurements at a constant shear rate of 100 s^{-1}. A slow thermal cycle with a heating rate of 2.2 °C/min and a cooling rate of 1.2 °C/min was imposed in order to assure that the samples were adequately tempered. The complete measurement with the heating (up to 92 °C) and the cooling (down to 25 °C) ramps took around 90–100 min, without a dwell at the maximum temperature.

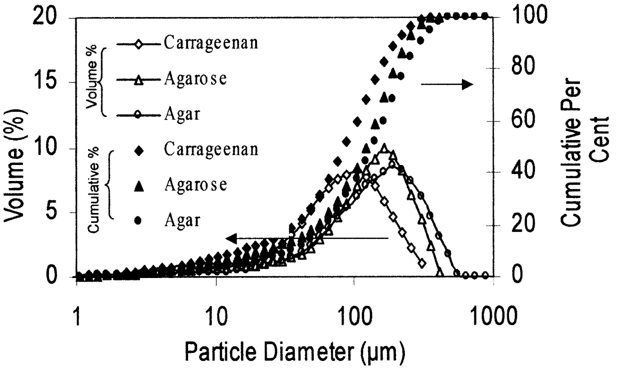

Fig. 3. Particle size distribution of the as-received powders of agar, agarose and carrageenan.

On dissolution a peak in viscosity is observed. Afterwards the viscosity decreases again and keeps nearly constant. This point has been considered as the dissolution temperature. Gelation temperature was considered as the temperature where the viscosity starts to increase.[23] The increase of viscosity on gelation was referred to as viscosity gap. Gelation hystheresis was calculated as the difference between the melting and the gelation temperatures.

4. Results and discussion

4.1. *Effect of binder concentration in the viscosity*

Figs. 4–6 show the evolution of viscosity with temperature for the different solutions of agar, agarose and carrageenan, respectively. Significant differences were found for the three polysaccharides, especially in the heating ramp.

During heating the agar solutions maintained a low viscosity up to ~60 °C, where the viscosity strongly increases peaking at ~75 °C, and decreases again at higher temperatures. This peak corresponds to the hydration of the gelling powders. On further heating (85±0.5 °C) dissolution of the hydrated molecules occurs, which is accompanied by a significant reduction in viscosity. On cooling, the viscosity of the solution maintains low until near the T_g, where a significant

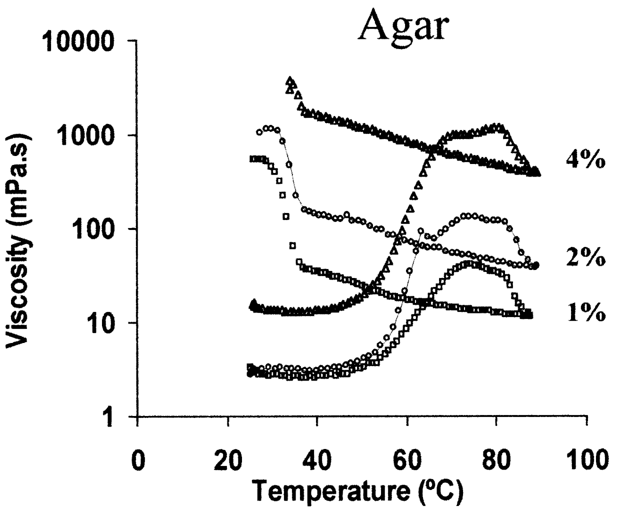

Fig. 4. Evolution of viscosity with temperature of aqueous solutions of agar at different concentrations.

increase occurs, corresponding to gelation. T_g seems to increase very slightly from 35 to 37 °C as the agar concentration increases from 1 to 4 wt.%.

In the case of agarose the same behaviour as for agar is observed both on heating and cooling. The increase of viscosity on heating is narrower than for agar although the temperature of dissolution tends to increase very slightly with binder concentration. The main difference on cooling is that the shift of the T_g values with binder concentration reduced.

For carrageenan the dissolution/gelation temperatures are very different to those observed for agaroids. Complete dissolution is reached at temperatures below 70 °C, that is, about 20 °C lower than required to dissolve agaroids. Furthermore, an increase of the dissolution temperature with concentration is evident (59, 65 and 70 °C for concentrations of 1, 2, and 3 wt.%). The maximum viscosity on heating is several times higher than the corresponding maxima registered for agaroids. This makes impossible to register the dissolution process in 4 wt.% solutions of carrageenan, as the maximum torque of the rheometer is exceeded. On cooling the viscosity increases rapidly below T_g, which is clearly dependent on the concentration of binder, changing from 32.5 to 48.5 °C for solutions of 1 and 3 wt.%, respectively.

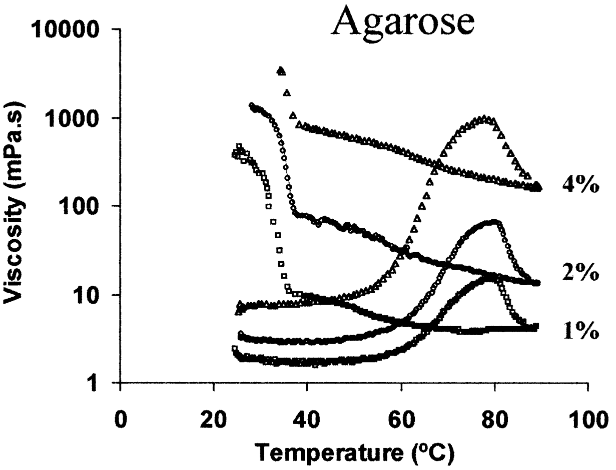

Fig. 5. Evolution of viscosity with temperature of aqueous solutions of agarose at different concentrations.

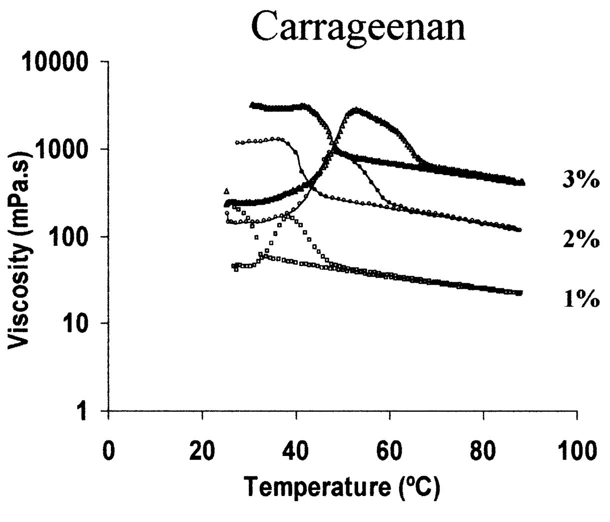

Fig. 6. Evolution of viscosity with temperature of aqueous solutions of carrageenan at different concentrations.

From these results the gelation hystheresis can be plotted as a function of the additive concentration, as shown in Fig. 7. For all studied additives the hystheresis between T_m and T_g keeps nearly constant with concentration. The hystheresis is much broader for agaroids, thus giving a broader working range. However, a clear advantage of carrageenan for ceramic applications is that dissolution requires a significantly lower temperature, so that it could be added as a powder to the ceramic slurry before heating the mixture at 60–70 °C, where the suspension remains stable. This is not possible for agaroids, because at the temperature necessary for complete dissolution (85–90 °C) the suspending liquid evaporates, leading to flocculation.

Fig. 8 plots the viscosity of aqueous solutions of the three additives at a temperature of 65 °C as a function of the solution concentration. The lowest viscosity is obtained for agarose, which allows an easier manipulation. The maximum viscosity is obtained for carrageenan solutions.

In addition to the viscosity of the hot solutions it is essential to study the gelling efficiency, which may be evaluated as the increase in viscosity or shear stress occurring on cooling below the T_g. Fig. 9 shows the viscosity gap occurring during the sol–gel transition as a function of polymer concentration. Obviously the gap is higher for increasing concentrations, being higher than 1000 mPa s for 2 wt.% solutions of the three additives.

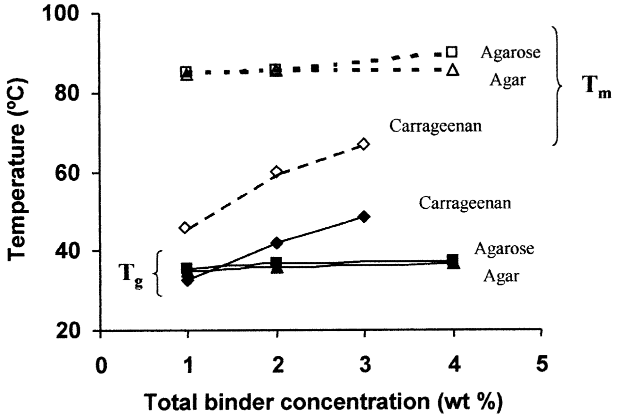

Fig. 7. Gelation hystheresis of the three additives as a function of concentration.

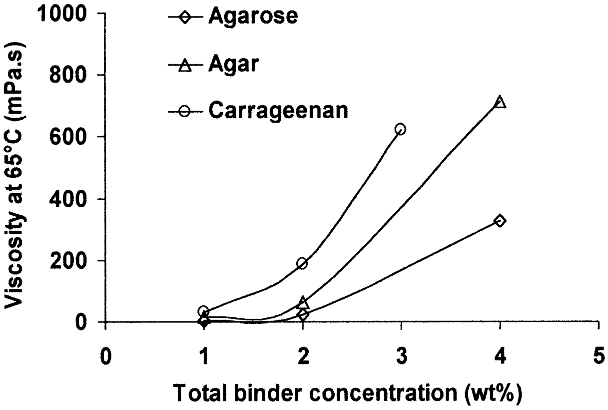

Fig. 8. Viscosity at 65 °C of the solutions of the three additives prepared at different concentrations.

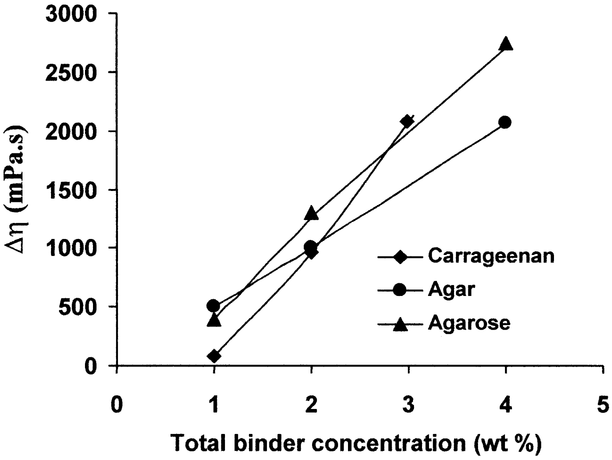

Fig. 9. Viscosity gap on cooling of the solutions of the three additives prepared at different concentrations.

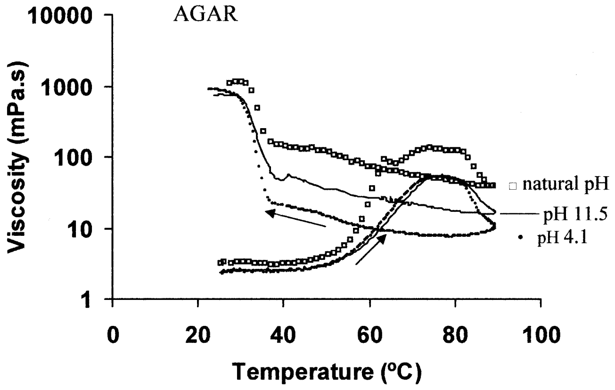

Fig. 10. Evolution of viscosity with temperature of 2 wt.% agar solutions with different pH.

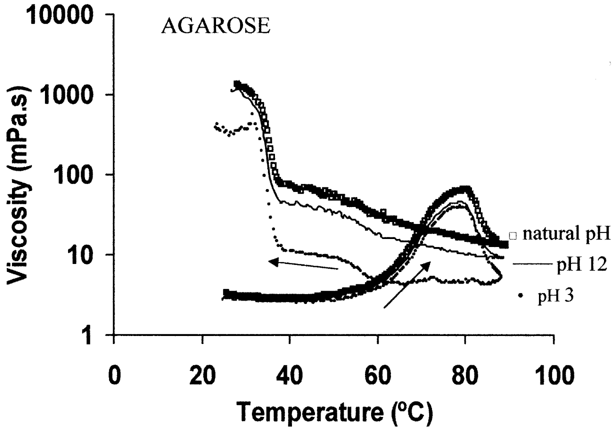

Fig. 11. Evolution of viscosity with temperature of 2 wt.% agarose solutions with different pH.

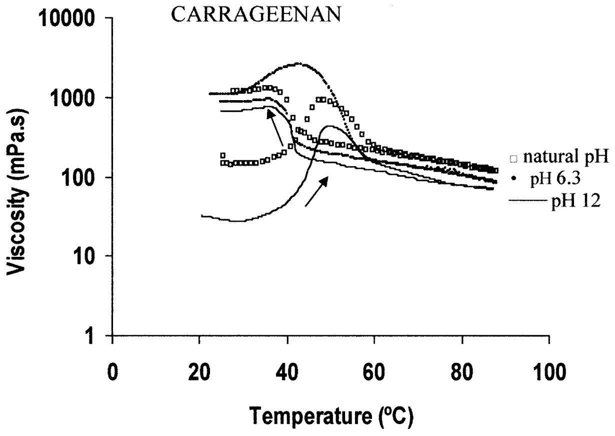

Fig. 12. Evolution of viscosity with temperature of 2 wt.% carrageenan solutions with different pH.

4.2. Stability of gelling additives with pH

A second aspect to be considered for ceramic applications refers to pH stability. Ceramic slurries can be prepared in a broad range of pH conditions. Usually, polyelectrolytes are preferred as they impose less agressive conditions (typically pH = 7–9). Therefore, it is essential to know wether the gelling binders maintain their properties at extreme pH conditions or not. For this study 2 wt.% solutions of each additive were studied in the same conditions of the previous experiments. The natural pH was around 6–7 and 10 for solutions of agaroids and carrageenan, respectively. The pH of the solutions was changed by adding either HCl or TMAH. Figs. 10–12 show the viscosity/temperature curves for agar, agarose and carrageenan solutions prepared to different pHs, respectively. In these curves important changes are observed, especially for carrageenans. In the heating ramp the increase of viscosity during dissolution is very high in acidic conditions and the temperature of maximum viscosity shifts down with respect to that for basic conditions. After dissolution a very low viscosity is obtained for any pH value. On cooling the Tg is not affected by pH, but the viscosity gap due to the sol-gel transformation changes. The natural pH gives slightly higher viscosity on gelling but the gap is sufficiently high in all cases to assure gelation. Consequently, it can be expected that when introducing carrageenan to a ceramic slurry it will provide the necessary gel-strength to allow manipulation after shaping for a pH range as broad as 4–12. It must be also noted that for suspensions dispersed with polyelectrolyte the resulting pH will be very near to the natural pH of the binder, where the gelling efficiency is higher.

In the case of agaroids the evolution of viscosity with temperature is much less dependent on the pH. The gelling efficiency is maintained in a broad margin of pH, between 3 and 12. The viscosity always increases during gelation at least 25 times.

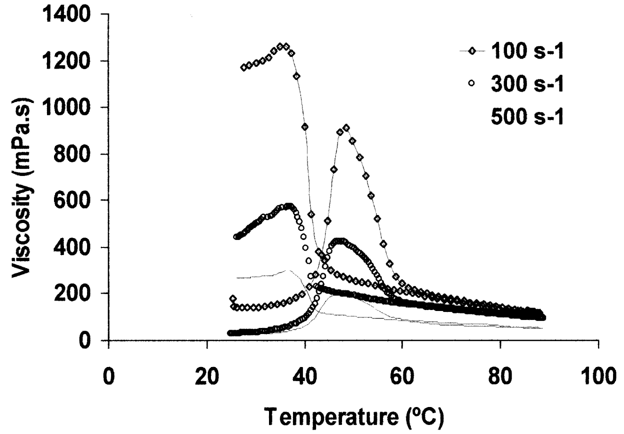

Fig. 13. Effect of shearing conditions on the viscosity/temperature curve for 2 wt.% carrageenan solutions.

4.3. *Effect of shearing on the* T$_g$

For characterizing the gelling binder solutions it is also interesting to determine how shearing can affect to the evolution of viscosity with temperature. This test was only performed for a 2 wt.% solution of carrageenan, since this compound was the unique affected by the previously studied parameters. Fig. 13 shows the viscosity/temperature cycles measured at constant shear rates of 100, 300 and 500 s^{-1}. The general shape of the curves keeps constant, although viscosity decreases with increasing shear rates, because of the shear-thinning behaviour of these solutions. The variation of the dissolution and gelling temperatures is negligible. Consequently, the main parameter to be controlled during forming operation is just temperature.

4.4. *Reversibility of the gels*

The studied binders are thermoreversible. A series of tests was performed to study this reversibility and to

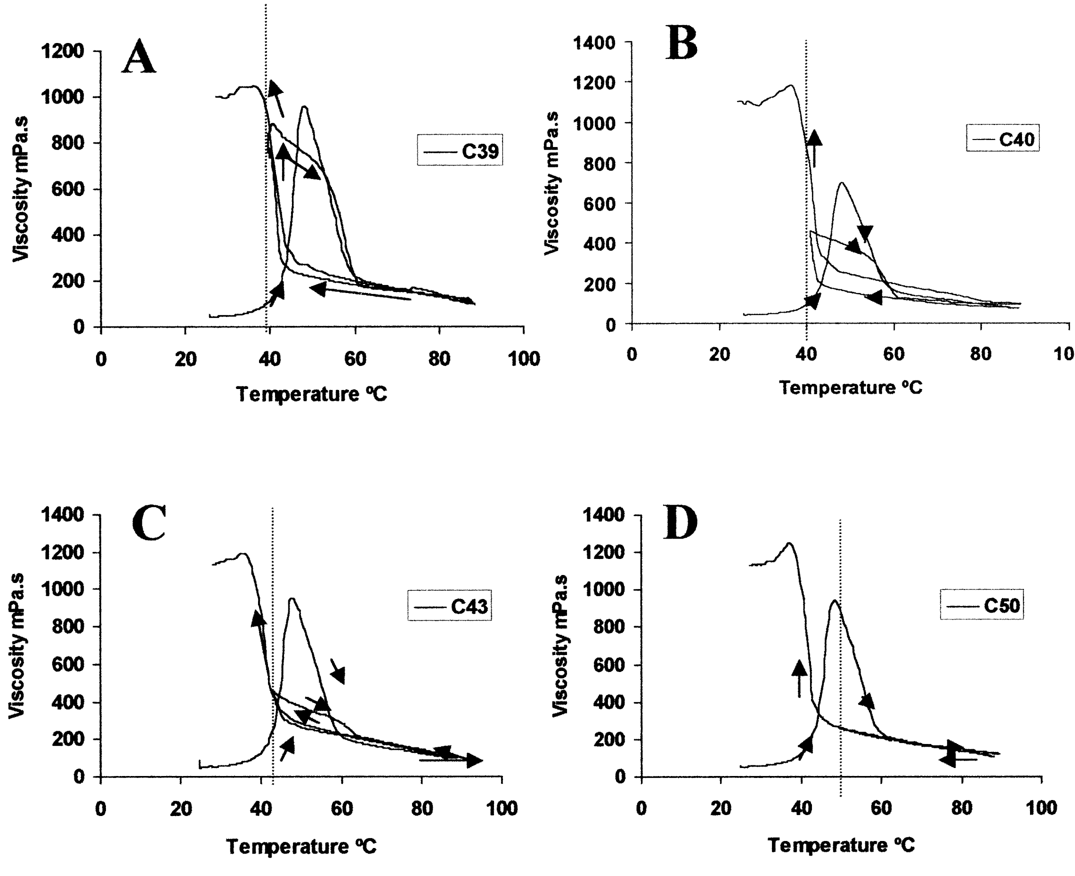

Fig. 14. Reversibility of the 2 wt.% carrageenan gels. The binder was first heated at 92 °C, then cooled at the marked temperature in each plot, reheated to 92 °C and finally cooled to room conditions.

determine the critical point of minimum temperature at which the solution can be maintained without significant changes on rheological properties and gel strength. This study is only presented for the 2 wt.% solutions of carrageenan, which shows the higher increase of viscosity during dissolution. Fig. 14 plots different sequencies of hystheresis temperature cycles. In all cases the carrageenan/water mixture is first heated at 92 °C and then cooled to temperatures of 39 °C (Fig. 14a), 40 °C (Fig. 14b), 43 °C (Fig. 14c), and 50 °C (Fig. 14d). After reaching these temperatures the solutions were reheated again to 92 °C and finally cooled at 25 °C. As observed in these sequencies some hystheresis is appreciated in figures a to c, while in Fig. 14d the second cycle perfectly overlaps with the first one. This means that temperature must be always higher than 50 °C to prevent gelation.

5. Conclusions

From the above results it can be concluded that agar, agarose, and carrageenan have important advantages for near-net shaping of ceramics in water. They form very strong gels, are easy to use and are effective at low concentrations. Carrageenan is completely dissolved at temperatures below 70 °C and dissolution temperature increases with the solution concentration. For agaroids, the temperature needed for complete dissolution is >90 °C, and it is practically independent of the solution concentration. T_g of carrageenan increases with the solution concentration, but gelation hystheresis maintains constant. Agaroids provide a higher hystheresis, thus giving a broader range of working conditions. All these additives maintain the gelling properties in a broad pH margin and are not affected by shearing if ones takes care to avoid turbulent flow that can promote bubbles formation. The gel strength can be modified by changing the concentration of the precursor binder solution, but this strongly influences the rheological properties.

Acknowledgements

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