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Formation of Gels in Ethylcellulose Solutions. An Interpretation from Dynamic Viscoelastic Results

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ABSTRACT: Dynamic viscoelastic measurements of the systems formed on cooling from solutions of ethylcellulose (EC) in three diester phthalates and one monoester phthalate are analyzed. Data obtained in the linear viscoelastic region indicate that diester solvents develop thermoreversible gels. We analyze the thermomechanical stability of the gels in terms of gel−sol transition temperature, T_{gs}, and breaking stress for rupture of the structure at constant temperature, σ_c. A maximum in tan δ has been detected below T_{gs} on heating, leading us to define what we call the T_i transition. Elastic modulus, T_{gs}, σ_c, and T_i increase as the size of the alcohol in diesters is increased. The increase of solvent molar volume and C═O polarization with the size of the alcohol leads to the hypothesis of a competition between polymer−polymer direct hydrogen bonding (involving ethylcellulose OH groups at the C-6 position) and polymer−solvent electrostatic interaction involving the same OH groups. In diester phthalates the presence of two carbonyl (C═O) for each molecule allows the solvent to act as a bridge between EC chains, in a way similar to that envisaged for PVC/diester systems.

Introduction

Despite the effort achieved in the past decades, it is recognized that the nature of the physical junctions involved in thermoreversible gels is less understood than the bonds that produce chemical gelation. Consider for instance the case of PVC-based gels, a system exhaustively studied for over 40 years which is still the subject of controversy, since the mechanism of gelation has still not been clearly elucidated. Besides the three classical models for tie points in physical networks,[1] hydrogen bonding, crystallites formation, and liquid−liquid phase separation, in view of the fact that gelation occurs only in certain solvents, a specific solvent−polymer interaction, to be defined in each case, must be also considered. As was stated more than 40 years ago by Bisschops[2] and has been commonly accepted more recently,[3−5] chain junctions are hindered by a good solvent and promoted by a poor solvent. However, as an example of the apparent discrepancies one can find in this field, we have to mention that Dahmani et al.[6] have demonstrated that solvent quality has little effect on gelation of PVC/diester systems. In this case what matters is the formation of a PVC−solvent complex, which is suggested to occur through electrostatic interactions between the hydrogen of the H−C−Cl bond and the oxygen of the carbonyl on the diester.

Mechanical and rheological properties of the gels, including compression modulus measurements and the determination of gel−sol transition temperatures through very simple experiments such as ball-drop method, have been analyzed to gain an insight into the origin of the gel network. At present, sound rheological experiments, like dynamic viscoelastic measurements, provide accurate data on gelation processes, shear elastic modulus, and thermomechanical stability of the gels. A molecular interpretation of the magnitudes of these parameters is usually a good help to disclose the nature of the tie points.

Hydroxyl groups in anhydroglucose unit of cellulose, forming both intermolecular and intramolecular hydrogen bonds, are assumed to be the cause of the rigidity and insolubility of this polymer.[7] The substitution of hydroxyl groups by functional groups, leading to what we call “cellulose derivatives”, may induce thermoreversible gelation in some solvents, as was observed more than 50 years ago by Doolittle for cellulose nitrate.[8] Particular attention has been paid to thermal gelation of methylcellulose and hydroxypropylmethylcellulose in aqueous solutions, because besides its industrial applications these systems show the unusual phenomenon of thermoreversible gelation upon heating.[9−14] The research carried out by Kondo[7,15,16] clarifies the hydrogen-bonding formation in cellulose molecules, showing that the hydrogen bond engaged in the hydroxyl groups at the 6-position of anhydroglucose plays an important role in gelation.

Notwithstanding research devoted to lyotropic solutions of ethylcellulose (EC), which has deserved several publications,[17−25] as far as we know no scientific information on thermoreversible gels based on this cellulose derivative has been available until now. In this paper we analyze the viscoelastic response of EC gels in three diester solvents, in an attempt to understand the mechanism of gelation and to contribute to reach a more general perspective on thermoreversible gels with data of a different system.

Experimental Section

The polymer used in this work is ethylcellulose with an ethoxyl content of 46%, Ethocel Med. 100, supplied by Dow Chemical. Its molecular weight is $M_w = 59\,000$ and its polydispersity $M_w/M_n = 2.1$, as determined in a Waters 150-C ALC/GPC gel permeation chromatograph.

Three diester solvents, di(2-ethylhexyl)phthalate (DOP), dibutyl phthalate (DBP), and diethyl phthalate (DEP), and one

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Table 1. Solubility Parameter and Molar Volume of the Solvents[a]

solvent	solubility parameter δ (MPa)$^{1/2}$	molar volume (mL/mol)	polymer concn (wt %)
DOP	16.2	398	0.5−10
DBP	19	265.5	0.5−10
DEP	20.5	198.7	1−10
EB	16.8	142.3	2−30

[a] The solubility parameter of EC is 21.1 MPa$^{1/2}$. C=O polarization increases with alcohol group size.

monoester, ethyl benzoate (EB), have been used. The polymer concentrations of the systems as well as some characteristics of the solvents are included in Table 1. Ethylcellulose dried in vacuo at 60 °C for 24 h is mixed with the solvent, and at a temperature of 180 °C, after stirring for 10 min taking special care to avoid solvent evaporation, a clear solution is obtained. Cooling from solution, elastic-like clear systems (as elastic modulus overcomes viscous modulus) are obtained, many of which obey the mechanical definition of a gel given by Guenet[26] (see Results).

Dynamic viscoelastic functions, storage and loss moduli and loss tangent, have been measured as a function of amplitude, temperature, and frequency, using both Couette (in a Physica Rheolab MC 100 rheometer) and cone−plate and plate−plate (Carri Med CSL 100) geometries. In both types of equipment, measured values are not accepted when no harmonic oscillations are detected. The choice of the geometry has been done considering that, in temperature and amplitude sweeps performed on gels, ideally the frequency should be as low as possible, to minimize the contribution of entanglement to solidlike response, but depending on the equipment a loss of precision can be noticed. Good agreement between reliable data obtained using different geometries is observed. A Physica Rheolab MC100 viscoelastometer with Couette geometry has been utilized to perform amplitude sweeps, between 10^{-3} and 1 at a temperature of 5 °C and a frequency of 1 Hz, as well as frequency sweeps in linear viscoelastic behavior conditions between 10^{2} and 10^{-3} Hz. Temperature sweeps have been performed in both Physica Rheolab MC100 and Carri Med CSL 100 viscoelastometers at 1 and 10 Hz. Although both types of equipment are able to detect the transitions that take place on heating, gel−sol transition temperatures T_{gs} (see Results) are better determined at 10 Hz, with parallel plates of 4 cm diameter geometry and a gap of 400 μm. The so-called T_i transition temperature, at which a maximum in the loss tangent is observed, is better detected by temperature sweeps at 1 Hz and starting at 5 °C, controlling the temperature by a Peltier system and using cone−plate geometry with 4 cm diameter and 1:58:00° angle for the lowest concentrations and 2 cm diameter and 4° angle for the most concentrated gels.

A Setaram C80-D calorimeter was used to study the gel melting at a heating rate of 2.5 °C/min.

Results

Figure 1 shows several examples of the variation of the storage (elastic) and loss (viscous) moduli, G' and G'', respectively, with frequency for EC in EB, DOP, DBP, and DEP solvents at a temperature of 5 °C.

It is observed that in the range of concentrations considered in this work $G' > G''$. In the EC/EB system both moduli decrease at low frequencies (even at a concentration of 30 wt %, not shown in the figure), whereas for the diester-based systems the response is typical of a gel network, neither modulus showing any significant frequency dependence. Although a certain elastic-like character (since storage modulus overcomes loss modulus) can be assessed to the EC/EB system, we note that this system does not accomplish the definition of a gel (see for instance ref 26), since both moduli tend to vanish as the frequency tends to zero. For the rest of the samples, based in diester phthalates, an elastic modulus can be defined.

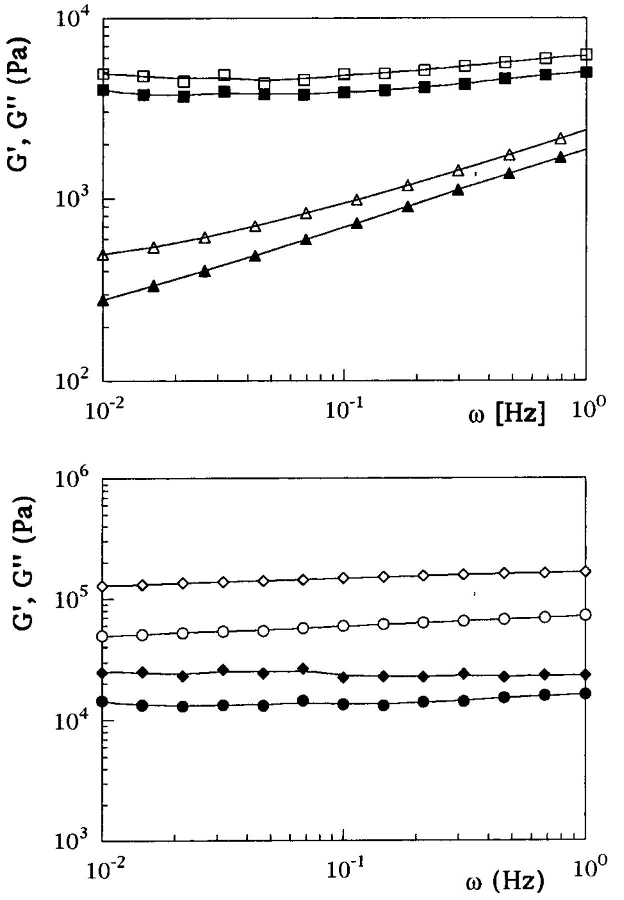

Figure 1. Storage (empty symbols) and loss modulus (full symbols) as a function of frequency, obtained under linear viscoelastic conditions for 10 wt % solutions: (◇) DOP (γ = 0.004), (○) DBP (γ = 0.004), (□) DEP (γ = 0.006), (△) EB (γ = 0.05).

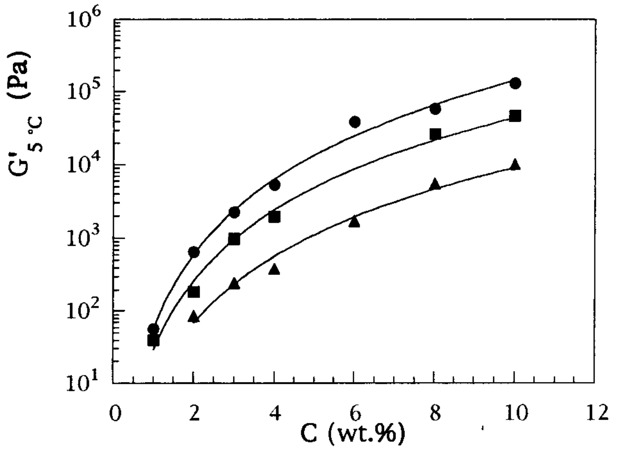

Figure 2. Frequency-independent elastic modulus taken in linear viscoelastic regime at a temperature of 5 °C as a function of polymer concentration: (●) DOP, (■) DBP, (▲) DEP. Lines are drawn to guide the eye.

In Figure 2 we present the variation of the elastic modulus $G'_{5°C}$ of gels, taken at a temperature of 5 °C, as a function of polymer concentration. We observe that the poorer the solvent is (compare solubility parameters of Table 1), the higher are the elastic moduli.

This result satisfies the general behavior observed in the literature when the role played by solvent in thermoreversible gelation of different systems is

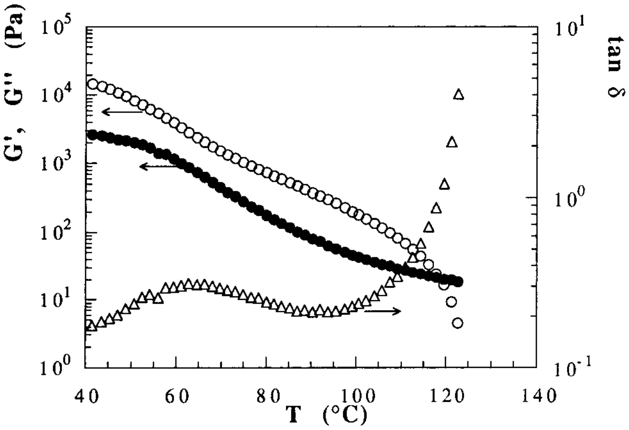

Figure 3. Temperature sweep results at a heating rate of 3 °C/min and a frequency of 10 Hz for 6 wt % EC/DOP gels. We define T_i as the temperature corresponding to tan δ maximum and T_{gs} as the temperature at which tan $\delta = 1$. (○) G', (●) G'', and (△) tan δ.

analyzed.[2−5] The data of Figure 2 and Table 1 also reveal that increasing the molar volume of the solvent, through increasing alcohol group size of the phthalate diester (DOP > DBP > DEP), enhances the elastic moduli of the gels.

Except in the particular case of thermogelation on heating, like for instance MC and HPC/water systems,[9−13,15] increasing temperature leads to the break of thermoreversible gels, reverting to the solution state. Dynamic viscoelastic measurements allow then to define a gel−sol transition temperature, as the temperature at which the loss modulus overcomes storage modulus and consequently the loss factor tan $\delta > 1$. An example of the mechanical response of our gels on heating is shown in Figure 3.

The rest of the gels display a similar behavior: we have been able to determine gel−sol transition temperatures, which we call T_{gs}, for all of them by means of this rheological technique. However, only a smooth baseline is observed by DSC, indicating that there is not a melting peak at the temperature at which tan $\delta > 1$. This result suggests that gelation does not arise from crystallization, even though a broad range of melting temperature or low crystal dimensionality could cause an absence of an endotherm.[27] We however disregard the hypothesis of imperfect or very small crystals, since actually gels are clear. This lack of crystallinity is probably a consequence of the high degree of substitution of our cellulose derivative.

Figure 4 shows that the effect of solvent type and concentration on gel−sol transition temperature is the same as the effect of these variables on elastic modulus, suggesting the same comments on solubility and solvent molar volume as for Figure 2.

Besides the sharp increase of loss factor with temperature, when the elastic solid turns into a solution, in Figure 3 we remark the presence of a maximum in tan δ as G'' tends to approach G' at intermediate temperatures. The physical meaning of this transition is discussed below. To the difference of gel−sol transition which depends on polymer concentration, the temperature associated with the maximum in tan δ, which we call T_i, is independent of concentration but varies with solvent, as can be seen in Figure 5.

The following T_i values have been obtained for the different gels: 65 °C for EC/DOP; 35 °C for EC/DBP, and 25 °C for EC/DEP.

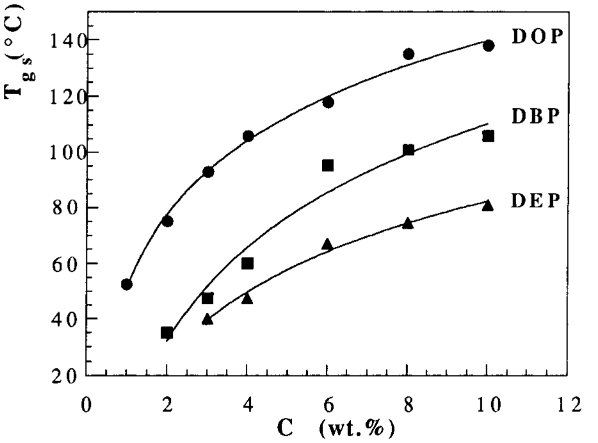

Figure 4. Gel−sol transition temperature as a function of concentration for gels based in different solvents. Lines are drawn to guide the eye.

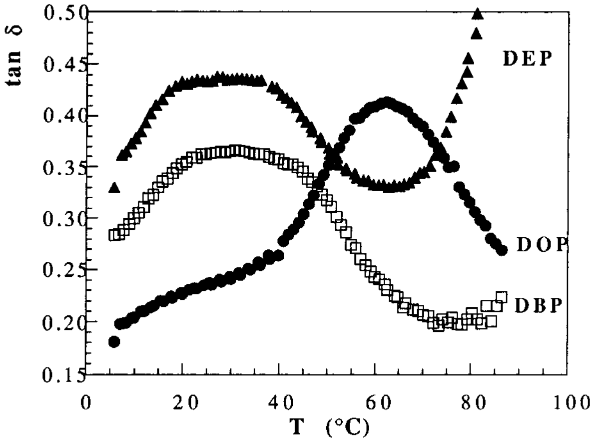

Figure 5. Effect of solvent type in tan δ maximum used to define T_i transition for 8 wt % gels, heating rate 3 °C/min, and frequency 1 Hz.

The mechanical stability of the gels is investigated analyzing the effect of shear stress amplitude, γ, on dynamic viscoelastic moduli. It has been reported in the literature that at large amplitudes ($\gamma > 1$) sinusoidal strains do not usually result in sinusoidal stresses (and vice versa): in such cases the property definitions for linear behavior (G', G'', and tan δ) are not meaningful for a nonlinear viscoelastic response.[28] However, we have to point out that in the range of amplitudes considered in our work (10^{-3} to 1) measurements were performed with harmonic oscillations of both stress and strain (see Experimental Section).

Typical results are shown in Figure 6 where it is observed that at low amplitudes elastic behavior prevails, but for a certain shear stress amplitude (which we call breaking stress, σ_c) loss modulus overcomes storage modulus, and a viscous dominant behavior takes place.

In Figure 7 we notice that breaking stress, which accounts for the mechanically induced fracture of the structure, increases with concentration and with alcohol group size of the phthalate (DOP > DBP > DEP), as both elastic moduli (Figure 2) and T_{gs} (Figure 4) do. On the other hand, when dynamic moduli are plotted against strain amplitude (not shown here), a critical shear strain, γ_c, can be defined analogously to σ_c defined in Figure 6. The physical meaning of both critical parameters is given by Holland,[29] who explains that

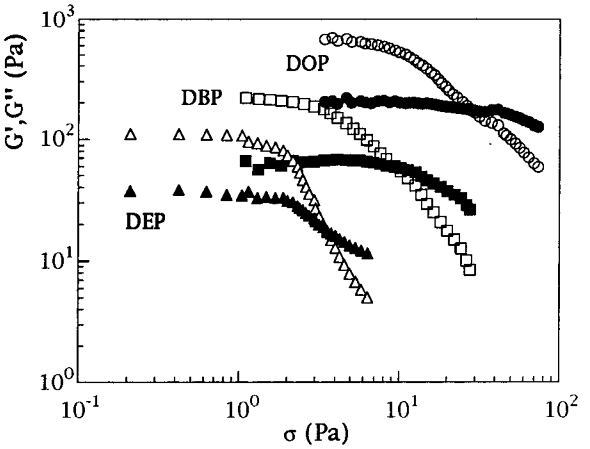

Figure 6. Shear stress amplitude sweeps for 2 wt % gels performed at a temperature of 5 °C and frequency 1 Hz. Empty symbols represent G' and full symbols G''.

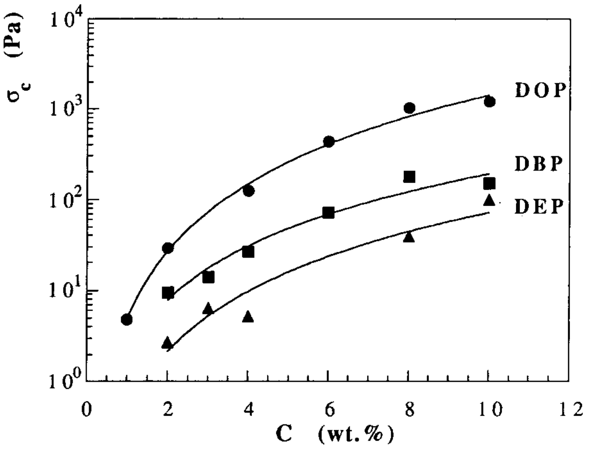

Figure 7. Effect of polymer concentration and solvent type on breaking stress σ_c. Lines are drawn to guide the eye.

when one tries to stretch three equivalent rubber bands, the critical deformation will be the same as that of a single rubber band, but the critical force will be 3 times greater. Although there is a certain scatter among γ_c data, we do not notice any effect of the solvent, which reveals the difference between both critical parameters: strain γ_c is associated with the break of one bond, whereas stress σ_c represents the energy necessary for the destruction of all the bonds involved in the gel.[30] Therefore, the nature of the bonds that break during transition seems to be the same, whatever the solvent used.

Since the three characteristic parameters of the gels, $G'_{5°C}$, T_{gs}, and σ_c, vary with concentration and solvent nature (Table 1) in a similar way, we have envisaged the possibility of performing master curves of these parameters using a reduced variable a_sc, where a_s is a shift factor that accounts for the characteristics of the solvent. The data of Figure 4 give rise to the master curve shown in Figure 8, with $a_s = 2.5$, 1, and 0.6 respectively for DOP, DBP, and DEP. Using the same values of the shift factor leads to the master curve of σ_c in Figure 9.

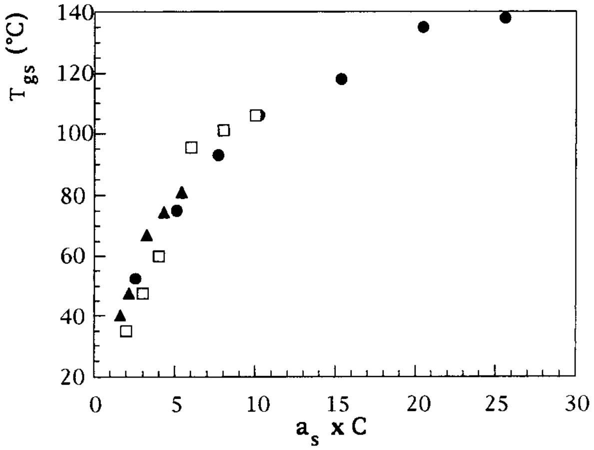

Figure 8. Master curve gathering the data of gel–sol transition temperatures of gels obtained with different solvents (see text): (●) DOP, (□) DBP, (▲) DEP.

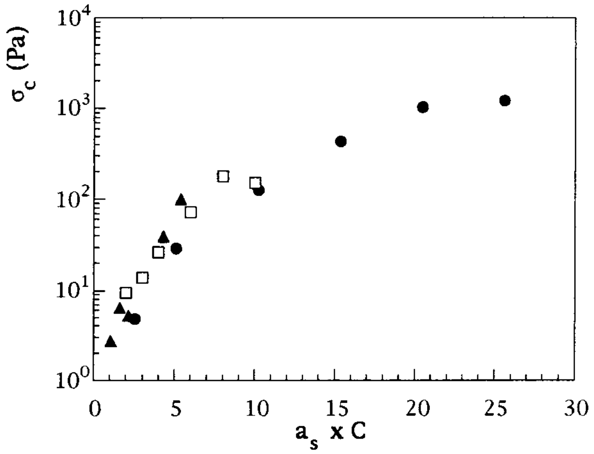

Figure 9. Master curve gathering the data of breaking stress of gels obtained with different solvents. The shift factors are the same as those of Figure 8 (see text). (●) DOP, (□) DBP, (▲) DEP.

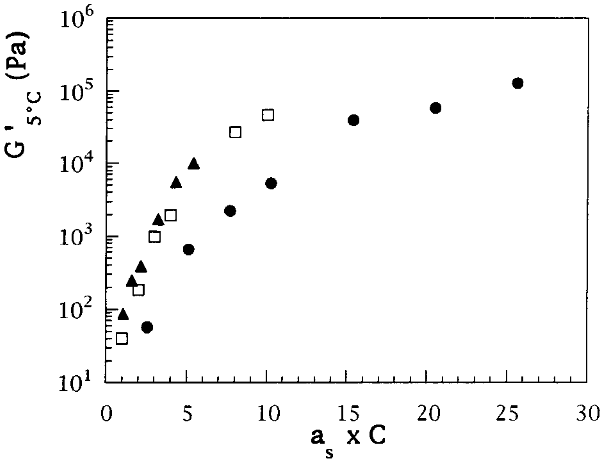

Figure 10. Elastic modulus data as a function of the reduced variable a_sC which accounts for the effect of the solvent. The values of a_s are those used in Figures 8 and 9 (see text). (●) DOP, (□) DBP, (▲) DEP.

This result seems to confirm that the same physical process (destruction of all the bonds involved in the gel network) lies behind gel–sol transition induced thermally or fracture induced mechanically. However, the attempt to gather all $G'_{5°C}$ data in a master curve, using the shift factors of Figures 8 and 9 for T_{gs} and σ_c, respectively, fails as can be seen in Figure 10.

This result suggests that another type of bond, the destruction of which can be associated with the T_i transition, must be considered to justify elastic modulus behavior, besides those associated with T_{gs} and σ_c.

Discussion

The theories of gelation developed during the past two decades[1,31,32] assume that, in systems which involve solvent molecules and monomers, the following particle−particle interactions take place: solvent−solvent, monomer−solvent, monomer−monomer van der Waals interactions, and monomer−monomer interactions leading to the tie points of the gel. The most characteristic physical parameters of the gels, like the elastic modulus and the gelation threshold at a certain temperature, depend on the probability that the interaction which leads to gelation is present between the two nearest-neighbor monomers. When this general picture is considered for EC/phthalate solvents, we have to bear in mind, on one hand, the well-known formation of intermolecular hydrogen bonds[15] in ethylcellulose chains and, on the other, the formation of solvent−polymer complexes when diesters are involved. In what the latter concerns, the specific interactions envisaged in some PVC gels, which imply a complex formation between the carbonyl group of diester solvents and the H−C−Cl part of PVC,[33−36] can be taken as a model for our EC gels. In this case as well, the monomer−solvent interaction arises from electrostatic effects, since EC hydroxyls are polarized so as to give a positive fractional charge of the hydrogen, $H^{\delta+}$, while the C═O bond of phthalate is polarized so as to give a negative fractional charge of the oxygen atom, $C{=}O^{\delta-}$. In the case of phthalate diesters the presence of two carbonyl (C═O) for each molecule allows the solvent to act as a bridge between EC chains. We remark that in both types of interactions ethylcellulose OH groups at C-6 are involved,[7,15,16] which leads to a competition between polymer−polymer direct hydrogen bonding, with a weight of $1 - \epsilon$, and polymer−polymer bonding through polymer−solvent electrostatic interaction, with a weight of ϵ.

The above-described scheme is used to explain our experimental results and in particular the effect of solvent characteristics on the elastic modulus and gel−sol transition. Actually, increasing the size of the alcohol in phthalate diesters (DOP > DBP > DEP) leads both the molar volume and C═O polarization to increase (Table 1). We first refer to the effect of molar volume. For the same concentration higher molar volumes mean fewer solvent molecules, which leads to a decrease of the weight ϵ of polymer−polymer bonding through solvent and therefore to an increase of the weight of polymer−polymer hydrogen bonding. Consequently, we can assert that the probability of forming intermolecular hydrogen bonds in EC systems increases with molar volume of the solvent. If we initially assume that tie points for network formation are of the hydrogen-bonding type (we will return to this point below), then the effect of molar volume on the competition between both type of interactions described above must be reflected in elastic modulus and gel−sol transition results. This hypothesis is confirmed by the results of Figures 2, 4, and 7 which show respectively an increase of elastic modulus, gel−sol transition temperature, and breaking stress at a constant temperature, with molar volume of the solvent (DOP > DBP > DEP). The effect of solvent type on gel−sol transition parameters, T_{gs} temperature and breaking stress σ_c, can be expressed through a shift factor that is unique for both parameters and allows to construct the master curves of Figures 8 and 9. This result is consistent with the hypothesis that considers that during the gel−sol transition EC intermolecular hydrogen bonds are broken, by either thermal or mechanical action.

However, the unsuitability of the shift factor used in Figures 8 and 9 to yield an elastic modulus master curve (see the scatter of data in Figure 10) leads us to consider the effect of the solvent also from the point of view of the enhancement of C═O polarization when the size of the alcohol in diesters is increased (DOP > DBP > DEP). Keeping in mind the above-described general picture on polymer−polymer and polymer−solvent interactions, we can imagine that, at sufficiently low temperatures (below T_i temperature defined in Figure 3), polymer−solvent electrostatic interactions occur, which due to the diester nature of the solvent leads to another type of polymer−polymer bonding, besides polymer−polymer hydrogen bonds. Therefore, according to our point of view, below the intermediate transition temperature, T_i, both types of interaction contribute to the elastic modulus; but above T_i only hydrogen bonds prevail, and the parameters T_{gs}, which define the gel−sol transition, depend exclusively on the molar volume. As mentioned above, C═O polarization increases with alcohol size of the solvent which leads to a stronger polymer−solvent electrostatic interaction: the dependence of T_i on solvent, observed in Figure 5, appears as a physical outcome of this hypothesis, since T_i(DOP) > T_i(DBP) > T_i(DEP). At this point we have to mention that the existence of a transition temperature below T_{gs} in PVC-based gels has been observed by dynamic mechanical thermal analysis DMTA[37,38] and DSC[35] and justified by the formation of complexes between PVC and the solvent.

Considering the results of Figure 1, we are compelled to analyze the role played by the monoester phthalate solvent, ethyl benzoate (EB), since EC/EB systems show a frequency-dependent modulus which is not the case for EC/diester phthalate systems. On one hand, we notice that this solvent possesses the lowest molar volume (Table 1) of the solvents considered in this work, although the main difference with respect to the diesters lies in the presence of only one carbonyl for each molecule, instead of two. This does not impede a complex formation between the carbonyl group of the monoester and ethylcellulose hydroxyls, but the capacity to act as a bridge between polymer chains, like in the diesters, is lost. We assume that only polymer−polymer direct hydrogen bonding can happen in this system. The low elastic moduli and its dependence on frequency, found even for high polymer concentration in EC/EB systems, are due to the chemical characteristics of the solvent and have two origins: (a) low molar volume which leads to a more advantageous position for polymer−solvent interactions, to the detriment of polymer−polymer interactions; (b) incapacity of the solvent to promote polymer−polymer bonding through polymer−solvent electrostatic interaction.

Since we have previously assumed that above the intermediate temperature, T_i, only interchain hydrogen bonding remains until gel−sol transition takes place, the G' and G'' spectra of the EC/diester system at a temperature T ($T_i < T < T_{gs}$) should resemble those of EC/EB at 5 °C of Figure 1.

This assumption is confirmed by experimental data displayed in Figure 11, which shows a dependence of the elastic modulus on frequency for EC/DOP system at 95 °C. This dependence is not observed at $T < T_i$, when polymer−polymer interactions through solvent

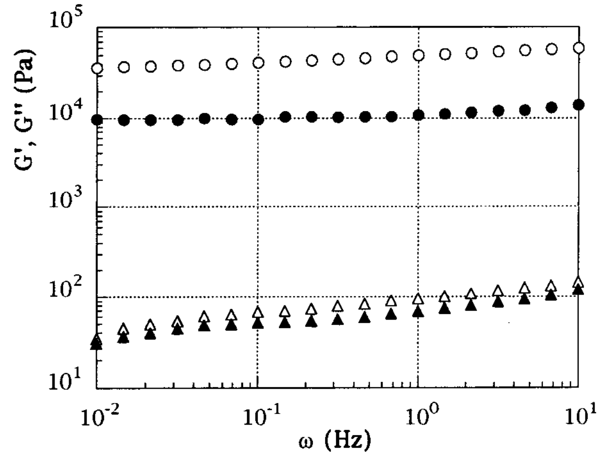

Figure 11. Storage (empty symbols) and loss modulus (full symbols) as a function of frequency, for a EC/DOP 6 wt % gel, obtained under linear viscoelastic conditions: (○) 5 °C and (△) 95 °C. $T = 95$ °C corresponds to an intermediate temperature between T_i and T_{gs}.

would be present besides polymer−polymer hydrogen bonds. The former type of interaction seems therefore to play a role in the formation of EC gels.

Conclusions

Cooling from EC/diester phthalate solutions, clear gels are formed, which is not the case for EC/EB (monoester phthalate) solutions. The analysis of the effect of solvent characteristics (molar volume and C=O polarization) on the elastic modulus and thermomechanical stability of the gels leads us to consider the hypothesis of a competition between polymer−polymer direct hydrogen bonding (which involves ethylcellulose OH groups at the C-6 position) and polymer−solvent electrostatic interaction involving the same OH groups. In diester phthalates the presence of two carbonyl (C=O) for each molecule allows the solvent to act as a bridge between EC chains, in a way similar to that envisaged for PVC/diester systems by Mutin and Guenet.[35] This is not the case, however, for the EC/monoester system, where polymer−solvent interactions may occur but not bonding between chains through solvent.

Taking into account this model our experimental results can be explained as follows:

(a) At low temperatures and amplitudes the mechanical response of EC/diester systems is typical of a gel network, since neither storage nor loss moduli depend on frequency. The dependence of dynamic moduli on frequency observed for EC/EB system seems to be a consequence of the incapacity of this monoester solvent to act as a bridge between polymer chains.

(b) Increasing the size of the alcohol in phthalate diesters enhances the elastic modulus of gels formed with these solvents. We consider that this reflects the increase of polymer−polymer hydrogen bonding when larger, but fewer in number, solvent molecules are involved. The increase of C=O polarization, associated with an increase of alcohol size, may also play a role, since chain bonding through solvent arises from electrostatic effects.

(c) The maximum in tan δ (corresponding to T_i transition), detected on heating below the gel−sol transition, shifts to higher temperatures as the size of the alcohol in diesters is increased. This transition is considered to be associated with the extinction of the links created through diesters: the dependence of dynamic moduli on frequency observed at $T_i < T < T_{gs}$ seems to confirm this hypothesis. A larger alcohol group gives higher C=O polarization, which produces more stable links.

(d) The gel−sol transition temperature, T_{gs}, and breaking stress at constant temperature, σ_c, can be fitted to master curves using the same values of a shift factor that accounts for the effect of the solvent. Assuming that above T_i only polymer−polymer hydrogen bonding remains, we consider that the gel−sol transition is associated with the destruction of these bonds.

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