

Investigation of the Elastic Properties of the Particle Network in Gelled Solutions of Hydrocolloids. II. Cellulose Microcrystals

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Synopsis

In order to obtain information about the particle network existing in gelled suspensions of cellulose microcrystals, the elasticity modulus was determined of series of dilutions of these gels. It was found that over a tenfold concentration range, the modulus varies as the 3.4 power of the concentration. A gel point could not be determined. A tentative model for this behavior is proposed, in which strong forces cause extensive linear aggregation, and weaker forces cause crosslinking of the linear aggregates. It is pointed out that this model is not unreasonable in the light of earlier experimental work on these gels. The results of similar experiments on gels of attrited level-off DP cellulose are also reported.

INTRODUCTION

In Part I¹ of this study we established that the elastic behavior of gels of the randomly coiled polymer carboxymethyl cellulose can be accounted for quantitatively by assuming that a network exists in which the molecules are linked together by noncovalent crosslinks, that this network may be described by the theories of Flory^{2,3a} and Stockmayer,⁴ and that it is deformed according to the theory of rubber elasticity.^{2b,5}

We have performed similar experiments with gels of cellulose microcrystals and the results are the subject of Part II. Some of the properties of cellulose microcrystals were recently described.^{6,7} The particles responsible for the formation of the gel have a rodlike shape; an axial ratio of 10 and a length of 0.4 μ are fairly typical. Suspensions of cellulose microcrystals are prepared from gels of microcrystalline cellulose; at concentrations of 0.5% or greater they are found to be gels. Gels of microcrystalline cellulose contain at most 30% of the material in the form of microcrystals, the remainder being present in the form of cellulose fibers of much larger dimensions, which alone are incapable of forming a gel.

Gels of cellulose microcrystals belong to the group of gels consisting of rigid asymmetric particles forming a network. Gels formed in clay suspensions also belong to this class. These gels are distinguished from those

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existing in solutions of "gums," such as those of carboxy methyl cellulose,¹ by the fact that once they are made to flow, they are much less viscous than the latter. Furthermore, some of the gels containing rigid particles are thixotropic, i.e., become very fluid upon stirring and thicken only slowly upon standing. The flow properties of these gels, whether thixotropic or not, are not well understood.⁸ It is obvious that a description of the flow would have to be based on a model of strongly interacting particles and that as a prerequisite to a quantitative description of the flow a knowledge of the interactions existing in a resting gel would be needed. The experiments reported in the present paper were designed to obtain information regarding this latter point.

EXPERIMENTAL

Materials

Gels of roll mill-attrited and of Rietz-attrited microcrystalline cellulose and gels containing only cellulose microcrystals were obtained as described before.⁷

Measurements

The shear modulus of the gels was obtained as described for gels of carboxymethyl cellulose in Part I.¹

RESULTS

The discussion of experiments of this type must be introduced by a description of the behavior of an individual gel under stress. It was found that if to any given gel a small enough shear stress is applied, the entire deformation is "instantaneous," i.e., takes place in a shorter time than that needed for our indicating instruments to register it. This deformation is immediately recovered upon removal of the stress and is proportional to the stress. Further, there is a range of stress in which, after the initial rapid deformation, a slow increase of the deformation with time is noted, although the entire deformation appears to be recoverable. The initial rapid deformation is still proportional to the stress, but the slow one varies with a higher power. Finally, above some fairly well defined value of the stress, the deformation is no longer fully recoverable; we call this value of the stress the yield stress.

As explained in Part I,¹ the fact that the shear may be fully recovered at low stresses means that the crosslinks in the network have not "wandered" during the measurement. It is necessary to make this point, since the crosslinks break and form rather easily, as is evident from the ease with which the gel may be made to flow and with which it forms again after flow.⁷

The modulus of elasticity is, of course, equal to the ratio of the stress and the shear. The maximum value of the recoverable shear is rather

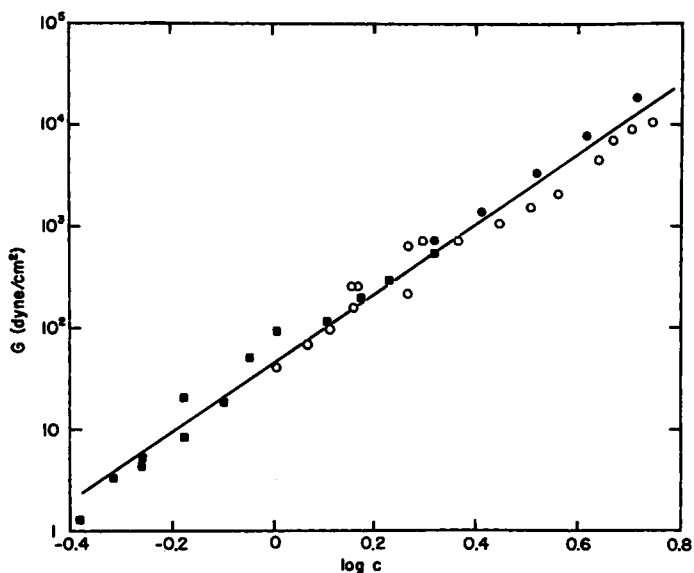


Fig. 1. Moduli of elasticity for gels of cellulose microcrystals in water. The concentration is expressed in grams per 100 ml. Different symbols indicate measurements on serial dilutions of three different samples. The straight line was drawn to fit the points.

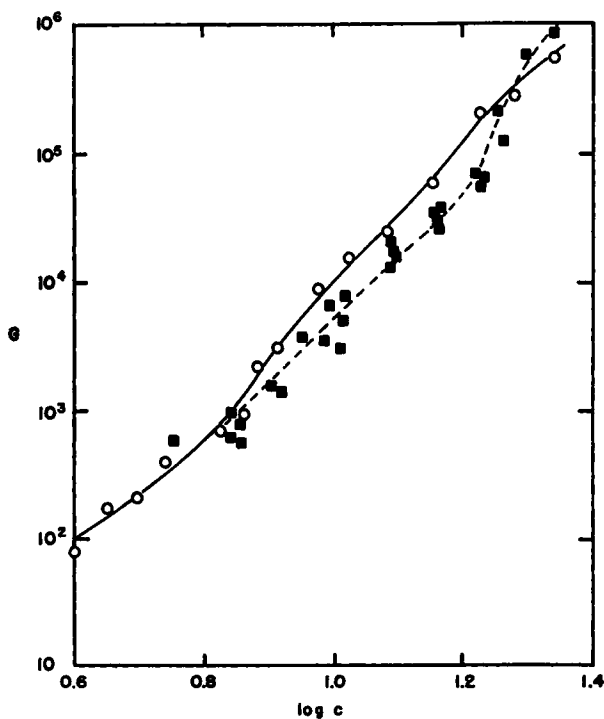


Fig. 2. Moduli of elasticity for gels of attrited level-off DP cellulose: (■) roll mill-attrited and (O) Rietz-attrited. The curves have been drawn to fit the points.

small, much smaller than with the rubberlike carboxymethyl cellulose gels. Thus, the linearity of the stress-strain curve is hardly unexpected and should hold whatever model is assumed to account for the elastic properties.

The values of the modulus of three sets of serial dilutions of gels of cellulose microcrystals are shown in Figure 1. The measurements were carried to a lower limit at a modulus of 1 dyne/cm.². With more dilute solutions, reproducible measurements were not obtained. In our first experiments this was caused by the flocculation shown by suspensions less concentrated than 0.5% upon frequent handling. However, when the dilute solutions were freshly made up from a stock gel and discarded after the measurement, erratic results were still obtained. Of course, at these low concentrations the modulus is near the limit where we could determine it accurately with our instrument.

Figure 2 shows values of the modulus obtained for various dilutions of roll mill-atritted and of Rietz-atritted level-off DP cellulose. Apparently the two different methods of attrition gave only slightly different products, as is also evidenced by the fact that the flow curves of dilutions of these two samples are almost identical. These measurements were carried to samples of 4% concentration. More dilute samples are probably still gels, but in these the fiber fragments settle, and reproducible measurements are impossible.

DISCUSSION

The most striking aspect of the variation of the modulus of carboxymethyl cellulose gels with the concentration was the behavior observed¹ in the limit of quite high and at low concentration. At high concentrations G varies as c^2 , in agreement with our assumption that the crosslinking reaction is a dimerization equilibrium. At low concentration, on the other hand, a gel point is observed, i.e., a concentration at which G becomes zero because below this concentration no infinite network exists. Theory^{2,3a,4} leads one to expect a gel point at a concentration where the number of intermolecular links equals one half the number of molecules.

It would not be unreasonable to assume that similar considerations apply to gels of cellulose microcrystals. However, for one, the data of Figure 1 clearly show no evidence for the presence of a gel point in or just outside the concentration range studied; these values of $\log G$ versus $\log c$ can be approximated within experimental error by a straight line of slope 3.4. Now it may be argued that the region close to the gel point was not investigated by us and that a slope greater than 3.4 would have been found at concentrations below 0.5%, had the data been reproducible. While this is probably true, it is still unfortunate that means of determining the gel point thus escape us.

To investigate what can further be learned from the data of Figure 1, we may first consider the following. Given the average number of particle-particle links per rod, the number of active crosslinks in the network is known, as was discussed in Part I.¹ In order to obtain from the number of

crosslinks the elasticity modulus of a network formed by stiff rods, one must not use the theory of rubber elasticity, in which the deformation leads predominantly to a decrease of the entropy of the network.* We have shown that, instead, when the energy of deformation is much greater than the entropic term in the free energy change, the modulus is given by⁹

$$G = HN_c \langle 1/n \rangle \quad (1)$$

Here N_c is the number of chains per unit of volume; these are the active chains, i.e., those between crosslinks. They each consist of a number of rods linked together by noncovalent bonds, $\langle 1/n \rangle$, being the average over all chains of the reciprocal of this number. The form of the constant H depends on the type of microscopic deformation which determines the macroscopic, observable elastic behavior; this may be either a deformation of the rods themselves or else one of the bonds linking the rods together. When the segments of rod are deformed, but not the bonds,⁹

$$H = 3\pi E a^4 / 20l \quad (2)$$

E being the elastic modulus of the rods (here that of cellulose = 3×10^{11} cgs), and a and l , respectively, the radius and length of the segments.

Equation (1) is valid only when the average number of particles between crosslinks is large. Since this should already no longer be the case at concentrations three or four times greater than the gel point,¹ it is important to note that for high degrees of crosslinking G should approach $E d$, i.e.,

$$G \sim E d \quad (3)$$

where d is the volume fraction of the cellulose in suspension.¹⁰

Turning now to the experimental data, it is seen that the modulus is only 10^4 at a concentration of 5%. This is very much smaller than the value of G one obtains with eq. (3) for a highly crosslinked network. Nevertheless, we have assumed that the linking of the rods is a bimolecular association reaction between equivalent surface sites, and that, consequently, the number of links per rod is proportional to the concentration. Hence the number of links per rod should be equal to at least 5 at this concentration, since it is equal to 0.5 at the gel point ($c < 0.5\%$). Thus, we must conclude that this assumption is incorrect.

One reason why the simple hypothesis is not valid might lie in the fact that we are dealing with stiff rods. When a rodlike particle has been linked to the network, the unreacted sites are still available for further

* That rubberlike elasticity cannot account for our data can be seen as follows. With $G = 10^4$ for $c = 5 \times 10^{-2}$ and with a "typical" particle weight⁷ of 6×10^6 , the number of particles per cubic centimeter is $N_0 = (6 \times 10^{23})(5 \times 10^{-2}) / (6 \times 10^6) = 5 \times 10^{13}$, whereas the number of active crosslinks per cubic centimeter in a rubberlike network of this modulus would be $N_c = G/dT = 10^4 / (14 \times 10^{-17})(300) = 24 \times 10^{16}$, which is much larger. Since the particles are rigid rods, N_c should be much smaller than N_0 if the network is to behave as a rubber (by virtue of the ease with which the interparticle bonds may be deformed) and not as a material nearly as stiff as cellulose itself.

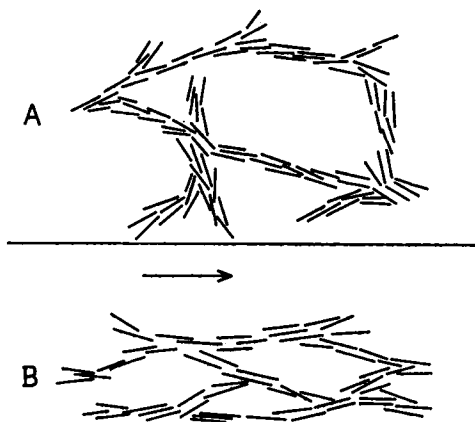


Fig. 3. Model for networks of cellulose microcrystals formed by almost parallel aggregation of rodlike particles. The aggregates are similar to sheaves, and the crosslinks in the network are formed by splitting and rejoining the different aggregates. Network *A* represents a gel in which the aggregates are oriented at random; network *B* a gel in which the aggregates have a nearly parallel orientation from a shearing motion which was applied to the solution before the gel was allowed to set. (The velocity gradient is perpendicular to the solution before the gel was allowed to set. (The velocity gradient is perpendicular to the arrow, and hence the aggregates are parallel to the arrow.)

linking but are restricted to given positions, much more so than the parts of a randomly coiled polymer which is linked to an infinite network. It is not clear, though, that this immobilization would lead to a sufficiently slow increase of the number of crosslinks per rod with the concentration to account for the low magnitude of the observed moduli.

Another possibility which we may consider is that the interparticle links are not all equivalent. In particular, we may consider a model in which two sites on each particle are much more reactive than the others. Very extensive aggregation would be the result, but the aggregates would not be branched or crosslinked. The introduction of additional less reactive sites on the rods would then allow crosslinking to take place; furthermore, almost every "secondary" link thus introduced would be an active crosslink. Retaining, then, the original hypothesis for the secondary links, we obtain the result that the number of crosslinks, N_c , is proportional to the square of the concentration, as is theoretically and experimentally found to be the case for carboxymethyl cellulose gels at high concentrations. As a result of this, the modulus will with eq. (1) vary approximately with the cube of the concentration over a considerable range, since the average value of n , the number of rods per chain, will be inversely proportional to the concentration.

When we consider the applicability of this model to the gels of cellulose microcrystals, we note that the dependence of G on c is predicted in an approximately correct way. Further, a somewhat realistic basis for assuming the existence of two types of quite diverse particle-particle links is provided by considering independent evidence that cellulose microcrystals tend to

aggregate side by side both in dilute solution¹¹ and upon precipitation with salt.¹² This behavior could indeed give rise to long aggregates containing many rods which would not necessarily form a network. The latter would be formed by the presence of another type of interparticle link. The weak links could, for example, be links between perpendicularly oriented rods. This behavior would also be shown if the primary links cause the particles to form slightly irregular (sheaflike) aggregates and if the crosslinks are formed by the splitting and joining of different sheaves. Such a network is schematically indicated in Figure 3A.

This model is particularly attractive, since it also permits one to give an explanation of the fact that a gel of cellulose microcrystals has a much higher yield stress when this is measured after a high shear rate has been applied to the gel.⁷ When the linear aggregates have been oriented to the streamlines, many more such crosslinks are possible than when the orientation of the aggregates is random. Such an oriented network is shown in Figure 3B.

We have thus provided an acceptable model to account for our data. The model should be regarded as tentative, and further experimentation with a material which does not possess the special properties of cellulose microcrystals appears desirable.

In conclusion, we would like to discuss our results with attrited level-off DP cellulose, which may be considered as a gel of cellulose microcrystals containing cellulose fibers as a filler, the latter forming 70% of the suspended material. Since the fibers alone form a coarse precipitate, it is to be expected that the microcrystals determine the behavior at low concentrations. Indeed, in Figure 2, moduli between 10^2 and 10^3 dyne/cm.² are observed for gels approximately three times as concentrated as for gels of cellulose microcrystals (Fig. 1). Since the modulus of the gels of unfractionated cellulose changes more rapidly with the concentration than that of the gels of microcrystals, it is apparent that at higher concentrations the hard-to-deform fibers take a more and more important part in the particle network.

The author is indebted to Dr. Robert Simha for discussions of and suggestions for this work. Further, he wishes to mention the experimental work done by Mr. N. J. Wegemer and Mr. A. G. Lankitus.

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Résumé

Dans le but d'obtenir des informations au sujet du réseau existant dans les suspensions colloïdales de microcristaux de cellulose, on a déterminé le module d'élasticité pour des séries de dilutions de ces gels. On a trouvé que au-dessus d'un domaine de concentration décuple, le module varie comme la puissance 3,4- de la concentration. Un point de gel n'a pas pu être déterminé. On propose un modèle expérimental pour ce comportement dans lequel des forces puissantes provoquent une aggrégation linéaire étendue et des forces plus faibles provoquant un pontage des agrégats linéaires. On a fait remarquer que ce modèle n'est par déraisonnable à la lumière d'un travail expérimental antérieur au sujet de ces colloïdes. On a aussi rapporté les résultats d'expériences similaires sur des gels de cellulose de DP limite soumis à des déformations mécaniques.

Zusammenfassung

Zur Gewinnung einer Information über das in gelierten Suspensionen von Zellulosemikrokristallen vorhandene Partikelnetzwerk wurde der Elastizitätsmodul von Verdünnungsreihen dieser Gele bestimmt. Über einen 10fachen Konzentrationsbereich zeigt der Modul eine Abhängigkeit von der 3,4ten Potenz der Konzentration. Ein Gel-punkt konnte nicht bestimmt werden. Versuchsweise wird ein Modul für dieses Verhalten vorgeschlagen, bei welchem starke Kräfte zu einer ausgedehnten linearen Aggregation führen, und schwächere Kräfte eine Vernetzung der linearen Aggregate bewirken. Dieses Modell erscheint im Licht früherer Versuche an diesen Gelen nicht unvernünftig. Weiters werden die Ergebnisse ähnlicher Versuche an Gelen aus abgeriebener Zellulose mit ausgeglichenem DP mitgeteilt.

Received March 6, 1964

Revised July 28, 1964