

Characterization of Small Gels in Viscose

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INTRODUCTION

The determination of the nature and properties of gels in viscose is a complex problem, and one that becomes highly important because such properties as filterability and spinnability are largely controlled by this factor. This paper will be concerned with the chemical and physical characterization of one class of gels in technical viscoses. The following paper will show the relationship between this class of inhomogeneity and the viscose filtration problem.¹

The literature of the studies of gels in viscoses is quite detailed. Manley and Bengtsson,² using light scattering techniques, have found that the gels in viscose have a particle molecular weight of 1×10^8 and are about 0.56μ in diameter.³ From the minimum in the intensity of the scattered light reported in Manley's paper² a diameter of 0.34μ can be calculated. This minimum is quite important, and will be discussed in greater detail below.

Parks and Jurbergs⁴ and also Kinsey and Mesek⁵ have employed an electronic counter, the Coulter Counter (Coulter Electronics Inc., Chicago, Ill.) in studies of the number and size of the gels in the range of 4-50 μ . Comprehensive reviews of the literature have been prepared by Treiber.^{6,7} A particularly important review paper has been published recently by Durso and Parks.⁸

The small gels in cellulose acetate solutions have been studied by Sperling and Easterwood.⁹ In that investigation the gels were characterized, by light scattering and electron microscopy, as being uniform spheres or potato-shaped objects of about 0.3-0.5 μ diameter.

The present study is an extension of the above investigation to the problem of small viscose gels. Light scattering, electron microscopy, and chemical methods have been combined, as before, to yield information about the size, weight, number, and chemistry of these objects.

EXPERIMENTAL PROCEDURES

Samples

The source of the celluloses and the type of viscose prepared are shown in Table I. These viscoses were all prepared from commercial pulps by simulated industrial methods. The samples usually were stored at 6°C.

for about 16 hrs. before use. Most of the viscoses were examined for one day only, although a few of the investigations took two days. In the latter case, all portions of the viscose were stored at 6°C. whenever possible during this period.

TABLE I
Designation and Description of Pulps and Viscosés

Designation	Description
A	Conventional process viscose from cotton linters pulp
B	Slurry process viscose from textile grade prehydrolyzed sulfate pulp
C	Conventional process viscose from tire cord grade prehydrolyzed sulfate pulp
D	Conventional process viscose from textile grade sulfite pulp

Gel Purification and Fractionation

Several different techniques have been developed for the investigation of the gels. All involve combinations of centrifugation and fractional filtration.

For electron microscopy studies, diluted viscose (ca. 1% cellulose) was passed through a 15 μ sintered-glass filter, to remove large gels, and then centrifuged at 90,000 g for 15 min. The impure small gels (main impurities: soluble viscose and NaOH) were redispersed in 0.1M NH₄OH with the use of a Mag-mix and recentrifuged at 60,000 g for 10 min. The purified gels were again redispersed in 0.1M NH₄OH, and an equal volume of

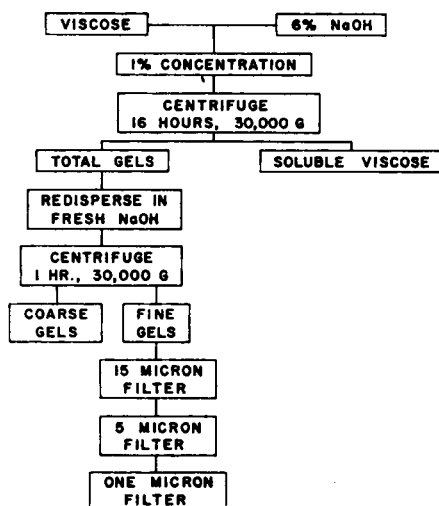


Fig. 1. Typical viscose gel fractionation procedure.

methanol was added to dehydrate the gels. Drops of this dispersion were suitable for electron microscopy.

It was found that the element of time is very important in the above procedure. The gels flocculate on standing, and delays of even a few hours after the initial centrifugation must be avoided.

The above procedure is also well suited for light scattering measurements. In this case observations were made before the addition of methanol. Or, an alternate procedure used for light scattering was to pass the diluted viscose through a $15\ \mu$ filter, carry out light scattering observations, centrifuge the viscose at 90,000 g for 15 min., and then reread the light scattering values. The difference in readings was assumed to be the intensity of light scattered by the gels.

A third procedure used in this investigation is outlined in Figure 1. Light scattering observations were carried out after the 15, 5, and $1\ \mu$ filtration stages. All the procedures and their variations for isolating and examining the gels were shown to be approximately equivalent; the method employed depended upon the purpose of the experiment.

Light Scattering

The Brice-Phoenix Model 1000D light scattering machine was used in this investigation. Its line-up and calibration are described in a previous publication.⁹

The equations for computing the weight-average molecular weight M_w the z -average diameter D_z , of the gels may be written:

$$H(c/\tau) = 1/M_w + 2A_2c \quad (1)$$

$$D_z^2 = 5(\lambda')^2(\text{slope})/4\pi^2(\text{intercept}) \quad (2)$$

where the (slope) and the (intercept) are determined from the Zimm plots.¹⁰ The wavelength of the incident light in the dispersion of concentration c is λ' ; τ is the turbidity, and A_2 is the second virial coefficient. For light having a wavelength of 5461 Å. *in vacuo*, $H = 5.05 \times 10^{-6}$, assuming dn/dc (the differential change in solution refractive index with solute concentration) is 0.212, which is the best value for soluble viscose.¹¹ This value was used for the present investigation as it is difficult to measure dn/dc on dispersed viscose gels directly. If the gels are largely of carbohydrate composition (see below), the error is not large.

The minima and maxima in the light scattering patterns were treated according to Debye's well-known relationship for uniform spheres:

$$\lambda'/D = k \sin(\theta/2) \quad (3)$$

The parameter k assumes values¹² near $4/3$, 1 , and $4/5$ for the first minimum, first maximum, and second minimum, respectively, of the scattering intensity at angle θ .

In order to obtain further information from the light scattering observa-

tions, an adaptation of the Shull and Roess small-angle x-ray formulation was also employed.¹²⁻¹⁴ The equation may be written:

$$\log(\tau/kc)_{c=0} = \text{constant} - (n + 4/2) \log [h^2 + (3/r_0^2)] \quad (4)$$

where $h = (4\pi \sin \theta)/\lambda$ and k may be either H or an arbitrary number, as explained below. The parameters r_0 and n are determined by trial and error by plotting $\log (\tau/kc)_{c=0}$ vs. $\log (h^2 + (3/r_0^2))$ and choosing different values of $\alpha = 3/r_0^2$ until a straight line is obtained. The slope of this straight line defines the value of n . The arithmetic mean of the diameters (number-average) is then given by:

$$D_n = (20/3)^{1/2} [\Gamma(n/2 + 1)/\Gamma(n/2 + 1/2)] r_0 \quad (5)$$

which equates the value r_0 to the diameter through the use of the gamma functions of n .

Electron Microscopy

The electron microscope employed in this investigation was a Phillips EM-75B. The electron micrograph grids were carbon coated and a drop of the above-described dispersion was placed on the grid and allowed to evaporate at room temperature. The gels were then shadowed with metallic chromium at an angle of ca. 30°.

Chemical Analysis

X-ray diffraction patterns were obtained on a Norelco unit. The resulting patterns were compared with photographs prepared at Buckeye from standard materials. Ultraviolet studies were carried out on a Beckman Dk-2 spectrophotometer unit. These were used for degree of substitution determination of the gels and an analysis for xylan content.¹⁵

EXPERIMENTAL RESULTS

Light Scattering and Chemical Analysis of Cotton Linters Viscose Gels

A cotton linters viscose was fractionated according to the procedure outlined in Figure 1. Light scattering readings were made after the 15, 5, and 1 μ sintered-glass filtration stages. A Zimm plot of the light scattering pattern obtained after the 15 μ filtration is shown in Figure 2. The sodium hydroxide solvent readings were, of course, subtracted from the gel dispersion reading. Note that the y -axis shows kc/τ rather than Hc/τ , k being an arbitrary number. This is because dry weights and light scattering determinations were generally made on separate viscoses. The use of an arbitrary k value does not alter the particle size determination by the slope-intercept method, but dry weight concentrations must be known before molecular weights can be evaluated. A particle molecular weight of 1×10^9 g./mole was obtained when the gel concentration had been determined by the dry weight method. One of the more troublesome

problems with this technique was that the quantity of gel appeared to differ somewhat from viscose to viscose.

The results of passing this sample of cotton linters viscose A through the procedure outlined in Figure 1 are shown in Table II. The D_{\min} values were computed from eq. (3) by use of the minimum in the light scattering intensity which occurred near $120\text{--}130^\circ$, as illustrated in Figure 2. The appearance of this minimum is usually due to the presence of monodisperse spheres, a conclusion that is also supported by the fairly close agreement of

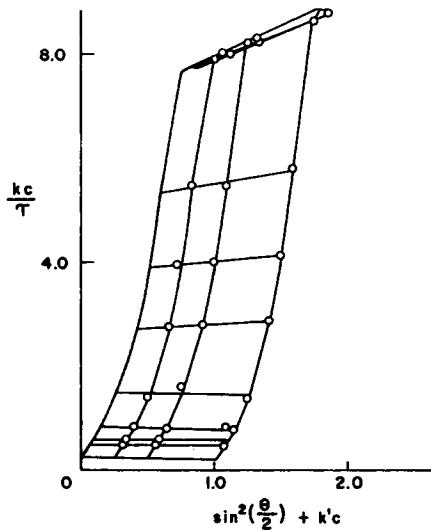


Fig. 2. Cotton linters viscose redispersed small gels, passed through $15\ \mu$ filter by process illustrated in Figure 1.

the values of D_z . Note that the z -average diameter of the gels has decreased only from 0.50 to $0.36\ \mu$ while approximately 72% of the material was removed. This decrease is due most probably to the removal of remaining traces of larger gels by the fractional filtration procedure. This removal apparently influences the slope-intercept D_z value more than the D_{\min} value, as would be expected.

TABLE II
Light-Scattering Diameters of Small Cotton Linters
Viscose A Gels

Filter, μ	D_z , μ	D_{\min} , μ	D (Shull and Roses), μ	Gels remaining, % ^a
15	0.50	0.34	0.27	100
5	0.45	0.34	0.28	85
1	0.36	0.31	0.17	28

^a Estimated from light scattering intensities at 90° .

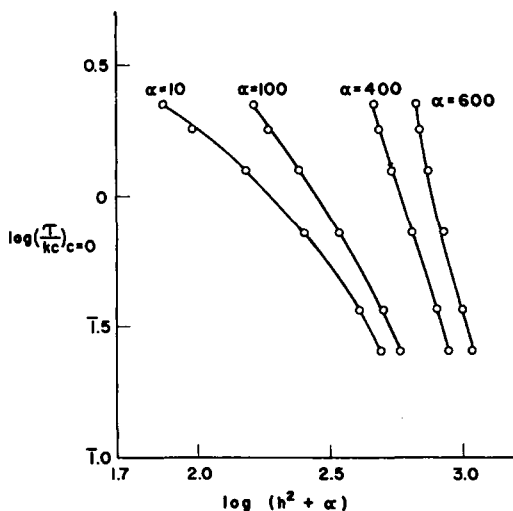


Fig. 3. Shull and Roess formulation applied to cotton linters viscose small gels.

It is difficult to account for the 72% drop in light scattering intensity by the removal of the larger gels only; i.e., some of the small spheres must have been removed also. It is rather surprising to find that gels of 0.3–0.4 μ in diameter were stopped by filter materials having pore sizes many times this size. This finding will be discussed in greater detail in the second paper in this series.¹

The Shull and Roess formulation was also applied to the light scattering data for comparison purposes. Typical results are shown in Figure 3 for the same data as those employed in Figure 2. Only the smaller angles (20–70°) were employed, however. The resulting diameters are shown in Table II. The values found are somewhat lower than the D_z values, as expected, and agree much better with the D_{min} values. This is probably because the Shull and Roess formulation yields a number-average diameter. The data as a whole provide evidence that the system consisted largely of nearly monodisperse spheres and a few much larger heterodisperse particles.

When the Shull and Roess formulation was applied to some other viscose gel systems thought not to be as monodisperse (some wood pulp viscose gel systems), unrealistic values of n were found. Since the Shull and Roess formulation was derived for a Maxwellian size distribution, the highly skewed distributions sometimes encountered may have been responsible. For very narrow distributions, the assumption of a Maxwellian form is not so important.

The chemical analysis of these gels is shown in Table III. The small gels are seen by x-ray analysis to be primarily composed of xylan, with a trace of silica. The number of gels per gram of cellulose was computed from the particle molecular weight and the per cent small gel content.⁹

TABLE III
Chemical Characteristics of Gels in Cotton Linters Viscose

Gel fraction	% gel, cellulose-based	X-ray anal.	Gels/g. cellulose
Greater than 15 μ	0.10	Silica, xylan	—
Less than 15 μ	0.08	Xylan,* silica	5×10^{11}

* Other samples of this type have contained cellulose-II.

It is of some interest to note the comparative chemistry of the small gels in cotton linters acetates. It was found in that study⁹ that the gels, slightly clustered, had $M_w = 6.7 \times 10^9$, and composed 0.10% of the sample. These gels were primarily composed of small spheres 0.34 μ in diameter totaling 1×10^{11} gels/g. cellulose. They contained 9.9% xylose of the fraction that hydrolyzed in the chromatographic carbohydrate analysis.¹⁶ While the analyses are by no means identical, at least part of the difference in molecular weight and numbers can be accounted for by the fact that the acetate gels were partly interconnected. It is not known whether these gels have the same origin; however, this question will be discussed in greater detail below.

Wood Pulp Viscosities

The result for low-purity prehydrolyzed sulfate pulp B small gels is shown in Figure 4. For simplicity only the zero concentration part of the Zimm plot is illustrated. Numerical data are summarized in Table IV. The particles are seen to be slightly larger than the cotton linters gels, but

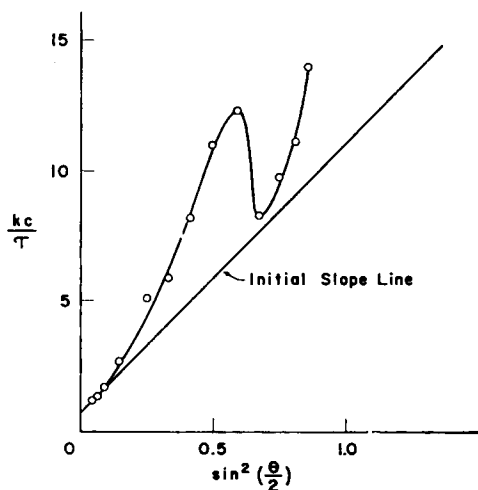


Fig. 4. Viscose B small gels. Zero concentration plot of 5 μ filter minus 1 μ filter.

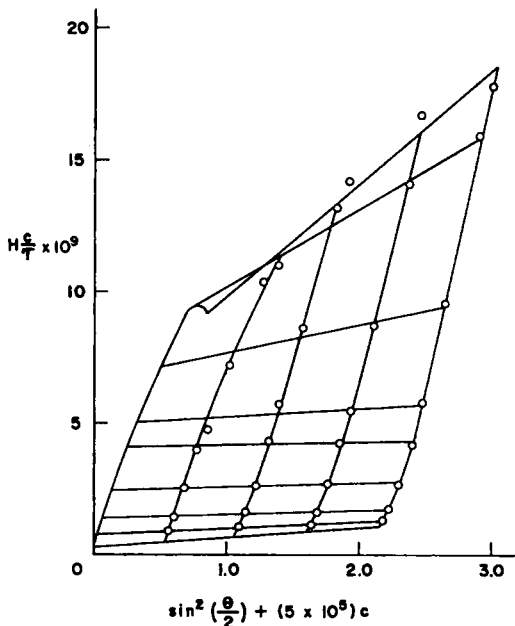


Fig. 5. Zimm plot of viscose D small gels. 15μ filtered minus centrifuged 90,000 g, 15 min.

appear to be just as monodisperse, as evidenced from the appearance of both a maximum and a minimum in the light scattering pattern.

Corresponding values for viscose C small gels show a slightly larger size and a considerably higher molecular weight than the viscose B gels. The difference in the molecular weight shows up most sharply in the computation of the number of gels/g. cellulose. Viscose C is much cleaner than viscoses B and D, as illustrated by the weight data.

The Zimm plot for the sulfite wood pulp small gels is shown in Figure 5. The size is seen to be slightly larger again, with a D_z value of 0.83μ . However, there is only a faint indication of a minimum in the turbidity, and that only at zero concentration. One might be drawn to the conclusion that these gels are more polydisperse for this system. As will be shown in the electron micrograph study, there is some evidence that these gels are actually slightly smaller, but are partly aggregated.

TABLE IV
Characteristics of Wood Pulp Viscose Small Gels

Vis- cose	M_w	D_z, μ	D_{min}, μ	% gel	No. gels/ g. cellulose	Elect microsc. D, μ
B	5.5×10^8	0.55	0.40	0.031	$4. \times 10^{11}$	0.10
C	8.6×10^8	0.72	0.40	0.012	8×10^9	0.11
D	2.5×10^9	0.83	—	0.043	1×10^{11}	0.06

Electron Microscopy

The small gels from viscoses A, B, C, and D were examined by the technique described under Gel Purification and Fractionation. The results are shown in Figures 6, 7, 8, and 9, respectively. The magnification of viscose B is $27,750\times$; the others are $23,375\times$ actual. The number-average diameters estimated from these photographs are tabulated in Table IV. In each case the gels are seen to be nearly monodisperse spheres. Viscose D gels are thought to be partly aggregated. This may account for the somewhat different light scattering values obtained from this viscose.

It is instructive to compute the diameters corresponding to the light scattering molecular weights. If a spherical shape having a density of

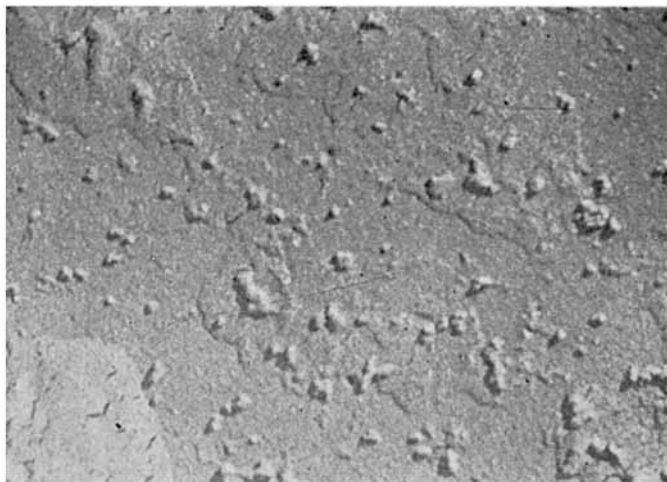


Fig. 6. Viscose A small gels. $23,375\times$ actual.

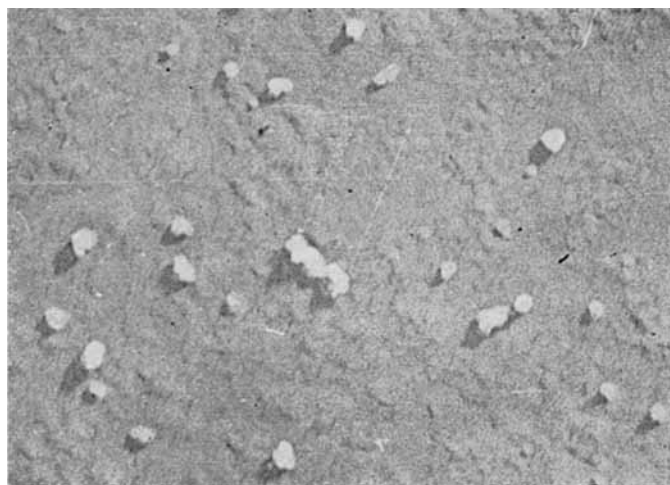


Fig. 7. Viscose B small gels. $27,750\times$ actual.

1.5 g./cm.³ is assumed, then a particle molecular weight of 5.5×10^8 (viscose B) corresponds to a diameter of 0.10 μ . This agrees well with the electron microscope diameter. The value for viscose C small gels corresponds to a diameter of 0.26 μ , considerably larger than predicted. It may

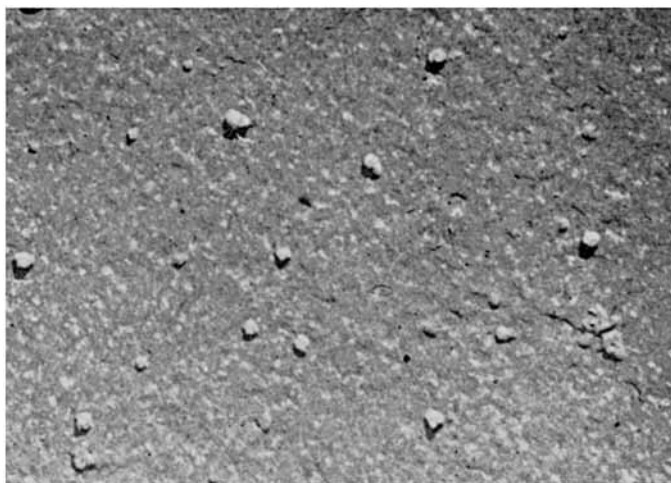


Fig. 8. Viscose C small gels. 23,375 \times actual.



Fig. 9. Viscose D small gels. 23,375 \times actual.

be that because of the unusually small quantity of small gels in this viscose, the larger gels were able to influence the slope and intercept values more than expected. From these calculations one may conclude that the gels are swollen in the dispersed state about three or four times their actual diameter. The constancy of swelling found in these experiments leads to speculations of whether or not these gels are crosslinked.

One point deserves special mention. These small gel samples all contain some larger particles, as is readily observed by Coulter Counter and microscopy techniques. The reason they are not often seen in electron microscopy and light scattering studies lies in their relative numbers. Coulter Counter techniques⁴ estimate the number of gels greater than 4μ to be of the order of 10^6 gels/g. cellulose. The small spheres have a population of about 10^{11} gels/g. cellulose; therefore, one should find about one large gel for every 10^6 small ones.

The results obtained in this investigation may be compared to those obtained by Manley and Bengtsson.^{2,3} The sizes computed by the slope and intercept methods, as well as the appearance of the minimum in the scattering intensity in their Zimm plot, suggest that these gels are the same. Their particle molecular weights, however, are five times lower than any found in this investigation. Whether this difference is real or whether it is due to their unusual method of estimating concentrations is not known. Certainly, the correct estimation of concentrations is difficult, as was found in this investigation.

Manley and Bengtsson's sedimentation diagram suggests that their particle size distribution was broader than that obtained in the present investigation; however, their purification efforts were less intense, especially since no attempt was made to remove the larger gels and fiber fragments.

Chemical Analyses of Wood Pulp Viscose Gels

X-ray analyses of the small gels from all of the wood pulp viscoses showed only cellulose II, in contrast to the cotton linters viscose A small gels, which showed primarily xylan. The analysis for xylose¹⁵ was employed on gels from viscose B, in an attempt to find out whether xylan was really present if only in an amorphous form. No xylose was found in the gels. It was further estimated from this test that only about half of the sample was of carbohydrate composition (probably cellulose, noting the above x-ray results). Ultraviolet analysis of these gels (sample B) showed them to be substituted with xanthate groups to only about 10% of the extent of the soluble material.

The lack of xylan may be explained by the fact that xylan is somewhat soluble in the highly alkaline solutions employed in viscose preparation. For an unknown reason, however, the xylan in the cotton linters gels did not completely dissolve. The gels may be crosslinked, and this factor, in combination with the noncarbohydrate component, may make the gels less accessible to xanthation.

From the above experimental data, it may be concluded that all of the viscoses examined contain a population of nearly monodisperse, spherical gels. The diameters are $0.3\text{--}0.6 \mu$ by light scattering studies of dilute dispersions, while the diameters of the dry gels by electron microscopy are near 0.1μ . The difference is attributed to the swelling of the possibly crosslinked gels. The number of these inhomogeneities is very high, of the

order of magnitude of 10^{11} gels per gram of cellulose, yet they comprise less than 0.1% of the total mass involved.

Chemically, the wood pulp viscose small gels appear to be about half cellulose II of a very low degree of substitutions. The composition of the other half is not known. The cotton linters gels were different in this respect, containing xylan and some silica.

The results obtained in this investigation bear a striking resemblance to those obtained in the counterpart acetate gel study, both for the wood pulps and the cotton linters. The main similarities are the number, size, monodispersity, and swelling characteristics of the gels. The main difference seems to be in the chemical composition, the wood pulp acetate gels being very high in xylan. The lack of xylan in the wood pulp viscose gels may be due to its dissolving in the highly alkaline liquids employed in viscose preparation.

The above similarities suggest that the small gels from acetates and viscoses have a common origin. Investigation of this point is presently in progress.

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Synopsis

The small gels present in cotton linters viscose, prehydrolyzed sulfate wood pulp viscose, and sulfite wood pulp viscose were examined by light scattering, electron microscopy, and chemical methods. In all cases a population of nearly monodisperse, spherical gels was found. The diameters are 0.3-0.6 μ by light scattering techniques, while the diameters of the dry gels by electron microscopy are near 0.1 μ . The difference

is attributed to the swelling of the possibly crosslinked gels. The number of these inhomogeneities is very high, of the order of magnitude of 10^{11} gels/g. cellulose, yet they comprise less than 0.1% of the total mass involved. Chemically, the wood pulp viscose small gels appear to be about half cellulose II of a very low degree of substitution and about half of unknown composition. The cotton linters viscose gels contain xylan and some silica. These gels bear a striking resemblance to those studied in a previous acetate gel investigation, for both the cotton linters and the wood pulps. It is speculated that they may have a common origin.

Résumé

On a étudié par diffusion lumineuse, par microscopie électronique et par méthodes chimiques, la faible gelification de la viscose de fibres de coton et de la viscose de pulpes de bois préhydrolysés et le sulfite de viscose de pulpe de bois. Dans tous les cas, on trouve une répartition de gels sphériques quasi monodispersés. On obtient des diamètres de 0.3 à 0.6 μ par les techniques de diffusion lumineuse tandis que par microscopie électronique les diamètres de gels séchés sont proches de 0.1 μ . On attribue la différence au gonflement des gels probablement pontés. Le nombre très élevé de ces inhomogénéités est de l'ordre de 10^{11} gels par gramme de cellulose bien qu'ils occupent moins de 0.1% de la masse totale impliquée. Du point de vue chimique, les gels de la viscose de pulpes de bois semblent être composés pour une moitié de cellulose II de très faible degré de substitution et pour l'autre de composition inconnue. Les gels de viscose de fibres de coton contiennent du xylane et un peu de silice. Ces gels ont une ressemblance frappante avec ceux étudiés lors d'une précédente étude du gel d'acétate, dans le cas des fibres de coton et de pulpes de bois. Il semble qu'ils peuvent être d'origine commune.

Zusammenfassung

Die kleinen in Baumwollintersviskose, vorhydrolysierter Sulfat-Holzpulviskose und Sulfit-Holzpulviskose vorhandenen Gelteilchen wurden mit Lichtstreuung, Elektronenmikroskopie und chemischen Methoden untersucht. In allen Fällen wurden nahezu monodisperse, kugelförmige Gelteilchen gefunden. Die Durchmesser liegen nach Lichtstreuungsmessungen bei 0,3–0,6 μ , während die Durchmesser der trockenen Gelteilchen elektronenmikroskopisch zu etwa 0,1 μ bestimmt werden. Der Unterschied wird der Quellung der möglicherweise vernetzten Gele zugeschrieben. Die Zahl dieser Teilchen ist sehr hoch und beträgt grössenordnungsmässig 10^{11} Gelteilchen/g Cellulose; sie machen aber nur weniger als 0,1% der Gesamtmasse aus. Chemisch scheinen die kleinen Gelteilchen in Holzpulviskose etwa zur Hälfte aus Cellulose-II mit sehr niedrigem Substitutionsgrad zu bestehen, während die Zusammensetzung der anderen Hälfte unbekannt ist. Die Baumwollintersviskosegelteilchen enthalten Xylan und etwas Kieselsäure. Die Gelteilchen haben bei Baumwollinters und bei Holzpulps eine auffallende Ähnlichkeit mit den in einer früheren Arbeit über Acetatgele untersuchten Gelteilchen. Es wird vermutet, dass sie einen gemeinsamen Ursprung haben könnten.

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