The Effect of Softeners on the Elastic Modulus of Regenerated Cellulose Sheet

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INTRODUCTION

In the manufacture of commercial regenerated cellulose sheet, the presence of certain small molecules has been found to be essential to the achievement of flexibility and prolonged durability. Those with some lasting effect and also with humectant action are called softeners in the trade; these include glycerol and several glycols. It turns out experimentally that water is an excellent plasticizer for regenerated cellulose, but is not considered usually as a softener because it is fugitive.

In previous reports,[1,2] we have inquired into the chemical basis for softening action, using not only typical softeners but also other small molecules, e.g., ethylene carbonate, which might be expected to interact very little or not at all with cellulose,[1] and ethylenediamine, which might be expected to interact strongly.[2] All of these simple molecules, even including water, we have referred to as softeners; we hope that those who consider this to be deplorably loose nomenclature will pardon the fault on the grounds of convenience. Though water, ethylene carbonate, and ethylenediamine are quite impractical as softeners, of course, they do provide, when present, important clues to the fundamental nature of the plasticization of cellulose by added simple molecules.

The present work has been undertaken as a continuation of the basic study to provide a comparison between the nature of softener interactions and the effect of the added molecules on the mechanical properties of the film as indicated by the behavior of the elastic modulus.

This paper describes experiments on cellophanes softened with glycerol in which their elastic moduli were measured and compared with those of similar films containing no added substance other than water. The method and apparatus used for the modulus measurements will be described, and the results will be compared with those obtained for similar films containing ethylene carbonate and ethylenediamine.

Previous work on the elastic modulus of cellophanes and on cellulosic materials in general has shown that the elastic modulus decreases with increasing relative humidity.[3,4] Consequently, in this work the measurements were carried out at a series of constant relative humidities, and the amount of water present in the films was determined as well as the softener concentrations.

EXPERIMENTAL

Apparatus

The elastic modulus of cellophane has usually been determined either by using the equation relating the speed of sound in a material to its Young's modulus and its density[3,4] or by the vibrating reed method.[5] The measurements described here were carried out with an apparatus, especially designed for measurements on thin films, in which the cross-sectional area of the film specimen is determined in place.[6] The long specimens required for the sound velocity determination are avoided as well as the problems caused by the curling of the vibrating reed specimens, which may be especially serious in the case of films made of moisture-sensitive materials. The apparatus permits determination of the modulus corresponding to extension along any direction in the sheet. This advantage is shared by the sound velocity method and the vibrating reed method but not by such methods as the torsion pendulum.

The apparatus is shown in Figure 1. This apparatus consists of a phonograph recording head fastened to a heavy, shock-mounted frame. A small clamp is inserted into the needle holder of the recording head. The block on which the recording head is mounted may be easily rotated from the position in which this clamp is vertical to a position in which it is horizontal.
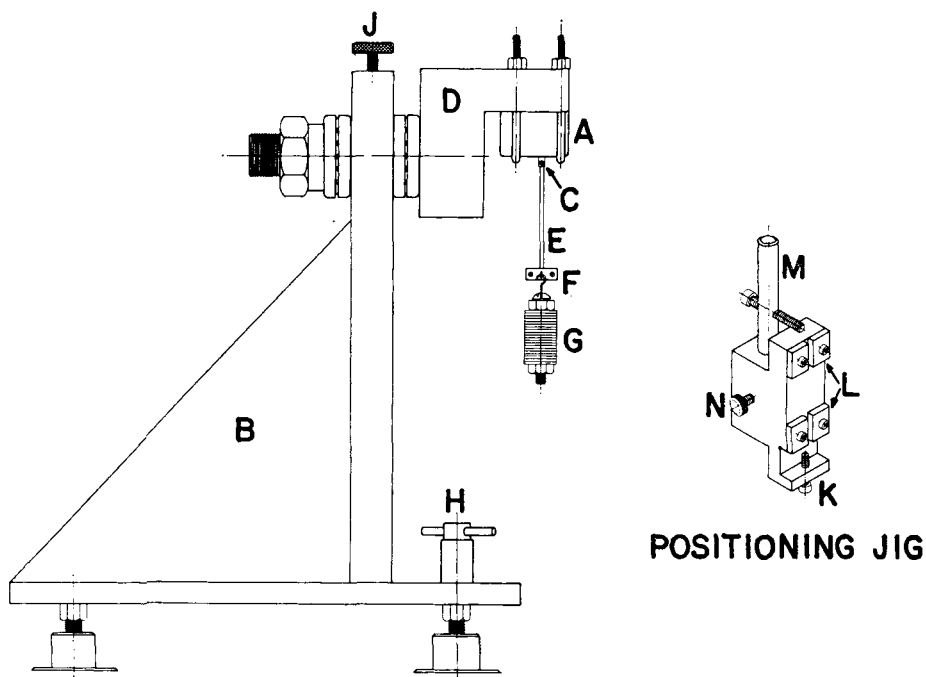
Fig. 1. Dynamic tensile modulus apparatus: (A) phonograph recording head (Astatic M-41-500); (B) steel plate frame; (C) clamp; (D) rotatable block; (E) specimen, 2 × 60 mm.; (F) lower clamp; (G) weight; (H) adjustable shock mount; (J) set screw for rotatable block; (K) set screw to hold lower clamp in jig; (L) guide blocks; (M) guide rod (permanently mounted on block D); (N) set screw to hold jig on guide rod.

The specimen is a strip of the film to be tested, 2 mm. wide and 60 mm. long. One end is held in the clamp in the recording head. The specimen itself supports the lower clamp and it, in turn, supports a weight which may be varied from 11 to 88 g. This weight is pivoted about the center of the lower end of the strip to insure a uniform tension across the width of the specimen. The specimen is placed in the apparatus by use of a jig which insures that the specimen is properly aligned for each measurement.

The lower clamp is placed in the jig and secured by means of a set screw, K. The specimen is placed between two pairs of guide blocks, L, and fastened in the lower clamp. The entire jig is then slipped onto a guide rod which is permanently mounted on the rotatable block holding the recording head. When the jig has been positioned so that the free end of the specimen is between the jaws of the upper clamp, the jig is fastened in place by a set screw, N, and the upper clamp is tightened. For stiff films, such as cellophane, it has been found necessary to slip a small piece of No. 50 cotton thread between one jaw of the upper clamp and the specimen to provide a uniform gripping across the width of the specimen.

After the specimen has been mounted, it is caused to vibrate transversely. The recording head is driven by an audio-oscillator whose frequency is varied until the specimen is observed to resonate. The resonant frequency for this vibration, f_{tr}, is given by the expression,

$$f_{tr} = (1/2l) \ (T/\mu)^{1/2}$$

$$= (1/2l) \ (mg/\rho A)^{1/2} \qquad (1)$$

Here l is the length of the specimen, T is the tension on the strip which is equal to the gravitational force on the weight, and μ is the linear density which is equal to the usual volumetric density ρ times the cross-sectional area A. (This is the principle of the Vibroscope which is used in the textile industry to determine linear density.[7] Thus eq. (1) shows that if we know the mass of the lower clamp assembly, the density of the film, and the length of the specimen, we may compute the cross-sectional area of the specimen. This treatment neglects the effect of the stiffness of the film on the transverse resonant frequency of the specimen. A correction has been derived for this effect[8] and is used in Vibroscope determinations on fibers. An examination of this correction shows it to be less than 1% for even the stiffest of the films studied here.

The recording head is then rotated 90° and the specimen is vibrated longitudinally. The resonant frequency for this type of vibration, f_l, is given by the expression,

$$f_l = (1/2\pi)\ (k/m)^{1/2}$$
$$= (1/2\pi)\ (EA/lm)^{1/2} \qquad (2)$$

Here k is the spring constant of the specimen, which is equal to EA/l, E being Young's modulus of the material, m the mass supported by the specimen, and l the length. Thus eq. (2) shows that the elastic modulus of the specimen can be computed from the resonant frequency combined with the cross-sectional area determined previously.

The length of the specimen was determined by allowing the specimen and the lower clamp to swing freely as a pendulum and timing the period of vibration. The length of the specimen was then found by calculating the theoretical length of the pendulum and subtracting the distance from the top of the lower clamp to the center of gravity of the lower clamp assembly. Combining the expressions for the two experiments just described we have an expression from which the elastic moduli can be calculated:

$$E = 0.1611\ \rho l^3 (f_t f_l)^2 \qquad (3)$$

Procedure

Preparation of Samples. A single uniform roll of 300-gage regenerated cellulose sheet prepared on a commercial machine at the Pisgah Forest, North Carolina, plant was used for preparing all samples. This gel film, never dried, was impregnated with the several softeners on a laboratory machine and dried to a finished moisture content of about 8%.

Uncoated films were prepared containing glycerol, ethylene carbonate, and ethylenediamine, each at three concentrations. Before and after the preparation of each series of three films containing one of these materials, a control sample was prepared containing no added materials other than water.

Conditioning of Samples. Specimens of the films to be studied were conditioned in rooms in which the relative humidity was controlled at 15, 35, and 81%, all at 75°F. In most cases the films were preconditioned at 35% R. H. Small pieces of the films were weighed after preconditioning, and again after final conditioning.

Measurements. After conditioning, specimens were cut for the modulus determinations in machine and transverse directions, for softener analysis,

and for the determination of the density. The density was determined by a sink-float method in which the density of a mixture of s-tetrachloroethane and o-dichlorobenzene was adjusted until the specimen became just suspended. The density of the final mixture was determined with a hydrometer. To avoid any error caused by density changes during the adjustment of the solution, the endpoint was always verified by adding a fresh specimen of the film. The modulus measurements were carried out in the room in which the specimen had been conditioned. Because of the variation of the modulus with humidity it was necessary to vary the weight on the lower clamp in order to keep the longitudinal resonant frequency approximately the same from one measurement to the next. The determinations reported here were carried out at resonant frequencies between 35 and 45 cycles/sec.

The moisture and softener contents of all films conditioned at 35% relative humidity were determined by chemical methods. The moisture contents of the small pieces cut prior to conditioning were found by the Karl Fischer method. The glycerol contents were determined by oxidation with periodic acid and back-titration with thiosulfate; the ethylene carbonate contents, by the dichromate oxidation method; and the ethylenediamine contents, by acid-base titration.

In the case of the glycerol films the moisture contents of the films conditioned at 15 and 81% R. H. were found from the changes in the weight of the small pieces weighed after preconditioning at 35% R. H. and again after conditioning at 15 or 81% R. H. The moisture contents of the ethylenediamine films were found by a similar method from the analytical results at each humidity for the ethylenediamine concentration. For the ethylene carbonate films, analytical results were used in all cases.

RESULTS

The results obtained for the glycerol-softened films and two of the films containing water only are shown in Table I. The quantity V_c which was calculated for each point is the volume of film containing one gram of cellulose, and is a measure of the swelling of the film. In the following discussion, we shall use the geometric mean of the moduli measured in the machine and transverse directions. According to Horio and Onogi[9] this quantity represents the mean value of the modulus of elasticity averaged over all angles. It should be noted

TABLE I
Properties of Films Softened with Glycerol

| Film | Relative humidity, % | $E \times 10^{-10}$ dynes/cm.² | | | Softener, moles/100 g. cellulose | | Density, g./cm.³ | V_c[a] |
		Machine direction	Transverse direction	Mean[b]	Water	Glycerol		
Control A	15	9.10	6.56	7.72	0.306	0	1.520	0.694
	35	8.49	5.78	7.01	0.453	0	1.510	0.717
	81	6.06	3.90	4.86	1.032	0	1.503	0.789
Control B	15	9.03	7.04	7.97	0.246	0	1.517	0.688
	35	7.80	5.67	6.65	0.530	0	1.500	0.730
	81	5.04	3.22	4.03	1.140	0	1.499	0.809
Glycerol, 7.3%	15	7.63	5.96	6.74	0.354	0.079	1.510	0.753
	35	6.95	4.96	5.87	0.556	0.079	1.502	0.781
	81	3.88	2.58	3.16	1.265	0.079	1.490	0.873
Glycerol, 13.7%	15	6.99	5.19	6.02	0.253	0.148	1.500	0.788
	35	6.29	4.27	5.18	0.475	0.148	1.497	0.816
	81	2.79	1.69	2.17	1.569	0.148	1.460	0.972
Glycerol, 21.3%	15	6.35	4.44	5.31	0.275	0.231	1.490	0.847
	35	5.41	3.54	4.38	0.517	0.231	1.482	0.881
	81	2.58	1.38	1.89	1.721	0.231	1.439	1.058

[a] $V_c = 100/(\rho \times \text{percentage of cellulose})$.
[b] Geometric mean of moduli in the transverse and machine directions.

that the geometric mean of the modulus in the machine and transverse directions in this series of measurements varies by a factor of 4, V_c by a factor of 1.5, and the glycerol content from zero to 21% by weight on a cellulose basis. Figure 2 shows the curves which result if the reciprocal of the modulus is plotted as a function of V_c, the volume of film containing 1 g. of cellulose. The displacement of the various glycerol curves from the water
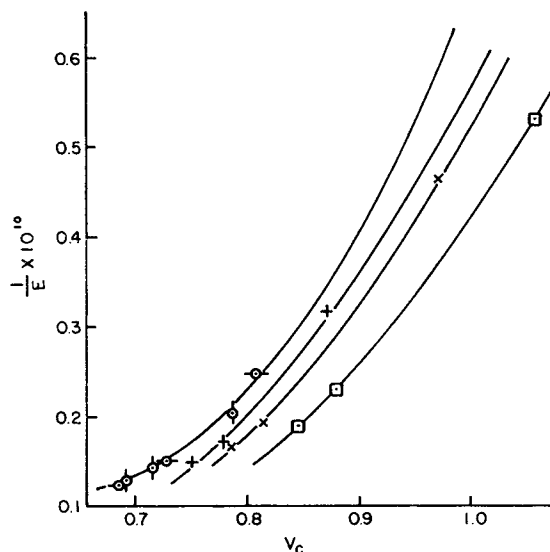
curve is a measure of the specific effect of glycerol. If the only effect of the softener were the disruption caused by swelling, these curves would coincide, since all films with the same V_c have their cellulose structures swollen to the same extent. The same volume of film contains 1 g. of cellulose in each case. The only difference lies in the nature of the materials other than cellulose which occupy that volume. Consequently the vertical distance of any point on a glycerol curve from the water curve is a measure of the effect of glycerol. It may be seen that swelling the cellulose to a given volume with water results in a softer film than does swelling it with water plus glycerol.

Fig. 2. Elastic compliance as a function of V_c, the volume of film containing 1 g. of cellulose: (◯) control A; (-⊙-) control B; (+) glycerol, 7.3% (×) glycerol, 13.7%; (□) glycerol, 21.3%.

TABLE II
Deviations of Young's Modulus Caused by Glycerol

Film	Relative humidity, %	Fractional deviation of E from water curve	Fractional deviation of E per mole glycerol per 100 g. cellulose
Glycerol, 7.3%	15	0.135	1.7
	35	0.163	2.1
	81	0.125	1.6
Glycerol, 13.7%	15	0.217	1.5
	35	0.237	1.6
	81	0.258	1.7
Glycerol, 21.3%	15	0.390	1.7
	35	0.397	1.7
	81	0.427	1.9

Table II shows that the ratio of the fractional displacement of the glycerol points from the water curve to the number of moles of glycerol present per 100 g. of cellulose is nearly constant. The fractional deviation was found by constructing a parabolic curve by the method of least squares through the six water points to obtain $1/E_w$ as a function of V_c. The value of $1/E_w$ corresponding to each glycerol point was then found from its V_c value. Because of the proportionality between the number of moles of glycerol and the fractional displacement from the water curve we now have an equation:

$$1/E = (1/E_w)(1 - 1.71M_{gl}) \qquad (4)$$

where

$$10^{10}/E_w = 2.144 - 2.642V_c + 4.811V_c^2 \qquad (5)$$

This equation fits the glycerol points with a standard deviation of 3% and the water points even more closely.

In the case of the glycerol films a comparison was also carried out between the values of the quantity $(1/EV_c^{2/3})$ and the number of moles of water and glycerol added to 100 g. of cellulose. This quan-

TABLE III

Corrected Compliances of Films Containing Glycerol and Water and Films Containing Water Only

| Film | Relative humidity, % | Moles water + 2 (moles glycerol) per 100 g. cellulose | $10^{10}/EV_c^{2/3}$ | |
			Measured	Calculated[a]
Control A	15	0.306	0.165	0.164
	35	0.453	0.179	0.179
	81	1.032	0.241	0.254
Control B	15	0.246	0.160	0.158
	35	0.530	0.185	0.188
	81	1.140	0.286	0.272
Glycerol, 7.3%	15	0.512	0.179	0.186
	35	0.714	0.200	0.210
	81	1.424	0.346	0.322
Glycerol, 13.7%	15	0.550	0.195	0.190
	35	0.771	0.221	0.217
	81	1.865	0.470	0.421
Glycerol, 21.3%	15	0.737	0.210	0.213
	35	0.979	0.248	0.246
	81	2.183	0.510	0.511

[a] Calculated from the equation obtained from data on controls A and B only and applied to glycerol films in the form:

$$\log(10^{10}/EV_c^{2/3}) = -0.8657 + 0.2626(M_{H_2O} + 2M_{C_3H_5(OH)_3})$$

tity, which we shall call the corrected compliance, represents the reciprocal of the stiffness in tension of a certain amount of cellulose regardless of the degree to which it has been swollen. If $\log(1/EV_c^{2/3})$ is plotted as a function of the number of added moles of glycerol plus water, a curve is obtained with considerable scatter. The glycerol points differed from the water points according to the amount of glycerol in the film, however, and it was found that when $\log(1/EV_c^{2/3})$ is plotted as a function of twice the number of moles of glycerol plus the number of moles of water per 100 g. of cellulose, the straight line shown in Figure 3 is obtained. An equation was obtained for the points representing the control films by applying the method of least squares to the logarithm of the corrected compliance and the number of moles of water. This equation is

$$\log(10^{10}/EV_c^{2/3}) = -0.8657 + 0.2626(M_{H_2O}) \qquad (6)$$

The agreement between the corrected compliances found for the glycerol films and the values obtained from this equation using $(M_{H_2O} + 2M_{C_3H_5(OH)_3})$ is shown in Table III. The coefficient 2 in this equation indicates that each mole of glycerol is twice as effective as a mole of water in softening the cellulose structure. This means that a molecule of glycerol is able to cause twice as much disruption in the cellulose structure as a water molecule because of its larger size and the presence of hydrogen bonding groups on both ends of the molecule.

The results obtained with films containing ethylene carbonate fall quite close to this curve if the simple sums of the number of moles of ethylene carbonate and the number of moles of water per hundred grams of cellulose are used as the abscissa values. These films lost considerable amounts of ethylene carbonate during conditioning at 35% and 81% R. H., as shown in Table IV which gives the moduli, compositions, and corrected compliances for two films containing ethylene carbonate. The last column of the table shows the values predicted by the corrected compliance curve obtained with the glycerol films (Fig. 3) but with a simple sum of the total number of added moles present per 100 g. of cellulose as the abscissa value.

Similar agreement is obtained with films containing ethylenediamine conditioned at 15% and 35% R. H. This result is shown in Table V. Here we have assumed that the diamine is present in the form of its monohydrate which is known to exist,[10] and the simple sum of the moles of the monohydrate plus the moles of the excess compo-

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TABLE IV

Properties of Films Containing Ethylene Carbonate

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| Film | Relative humidity, % | Softener, moles/100 g. cellulose | | Density, g./cm.[3] | $E \times 10^{-10}$, dynes/cm.[2] | | Corrected compliance, dynes$^{-1} \times 10^{10}$ | |
		Water	Ethylene carbonate		Machine direction	Transverse direction	Experimental	Calculated from total moles
Ethylene carbonate, 23.5%	15	0.300	0.190	1.502	7.04	4.91	0.195	0.183
	35	0.430	0.073	1.496	7.25	5.00	0.198	0.185
	81	0.692	0.012	1.503	5.52	3.43	0.277	0.209
Ethylene carbonate, 24.4%	15	0.315	0.185	1.501	7.40	5.15	0.186	0.185
	35	0.516	0.123	1.495	6.73	4.62	0.207	0.202
	81	1.183	0.007	1.480	4.61	3.08	0.301	0.283

nent (either water or diamine) is used as the abscissa value. The second column from the right shows the values of the corrected compliance predicted on this basis by the curve obtained for the glycerol films. The ethylenediamine films conditioned at 81% R. H. do not fall on this curve, however, unless the number of moles of diamine is weighted with a factor of 3.4 (or the monohydrate with a factor of 4.4), in which case good agreement is actually obtained. This may be caused by a high degree of disruption which becomes effective only at high degrees of swelling. It should be pointed out, however, that these particular films were conditioned only a few hours in order to avoid excessive loss of diamine at the high humidity and the films were presumably not in equilibrium with the surrounding atmosphere when the measurements were carried out.

Fig. 3. Corrected elastic compliance as a function of glycerol and water content; (⌽) control A; (–⊙–) control B; (+) glycerol, 7.3%; (×) glycerol, 13.7%; (□) glycerol, 21.3%.

Conclusions

From these results we conclude that the apparatus and methods described here are capable of providing useful information on the nature of the softening process in regenerated cellulose by water and other added materials. Our original results confirm the known fact that at each relative humidity the modulus of the films in equilibrium with that humidity decreases with increasing glycerol content. It should be noted, however, that only at 81% R. H. did the moisture content increase with increasing glycerol content. Therefore, the softening action of glycerol is presumably not caused simply by an increase in moisture content resulting from the presence of glycerol, but must be brought about by the disruption of the cellulose structure by the glycerol molecules.

A relatively simple treatment of these results has shown, furthermore, that when the cellulose is swollen to a given volume, the resulting film is softer if it is swollen by water alone than if it is swollen to the same volume by water combined with glycerol. At any given volume, the fractional decrease in reciprocal modulus resulting from the presence of the glycerol molecules seems to be proportional to the number of moles of glycerol present. This permits us to derive an empirical equation by which the moduli of these glycerol-softened films may be calculated quite accurately from their moisture and softener contents and their densities. This also permits us, however, to make several observations on the effect of glycerol on the elastic modulus.

We have seen, for instance, that the softening effect is not dependent on the degree of swelling alone, but that there is a specific effect of the added molecule. The proportionality between the decrease in compliance and the number of moles of glycerol means that there is a constant difference
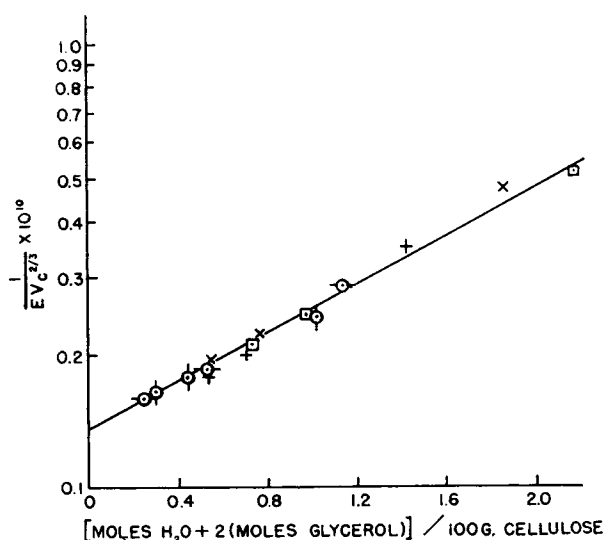
TABLE V
Properties of Films Containing Ethylenediamine

Film	Relative humidity, %	Softener, moles/100 g. cellulose		Density, g./cm.³	$E \times 10^{-10}$ dynes/cm.²		Corrected compliance, dynes$^{-1} \times 10^{10}$		
		Water	Ethylene-diamine		Machine direction	Transverse direction	Experimental	Calculated values	
								a	b
Ethylenediamine, 7.9%	15	0.332	0.132	1.482	8.64	6.28	0.162	0.166	
	35	0.589	0.105	1.474	7.83	5.26	0.182	0.196	
	81	1.673	0.115	1.456	2.93	1.75	0.460		0.486
Ethylenediamine, 11.1%	15	0.243	0.179	1.478	8.37	5.81	0.169	0.157	
	35	0.426	0.096	1.485	7.92	5.39	0.183	0.176	
	81	1.650	0.147	1.460	2.67	1.45	0.526		0.512
Ethylenediamine, 13.1%	15	0.158	0.214	1.464	8.14	6.06	0.166	0.154	
	35	0.488	0.121	1.483	7.59	5.15	0.188	0.183	
	81	1.648	0.174	1.472	2.50	1.28	0.577		0.543
	81	1.982	0.182	1.462	2.21	1.02	0.665		0.680

[a] Based on the assumption that ethylenediamine exists entirely as a monohydrate, this calculation uses the number of moles of hydrate plus moles of uncombined water or diamine present.

[b] A similar calculation based on 4.4 times the number of moles of ethylenediamine monohydrate plus the number of moles of water.

between the effect of a molecule of water and a molecule of glycerol. Therefore, we should expect that if we consider the effects of glycerol and water on a molar basis, we should be able to show that glycerol and water act on the cellulose structure in an exactly equivalent way.

According to the views of Nissan,[11,12] the elastic behavior of hydrogen-bonded materials is accounted for primarily by the stretching of these bonds and the change of the elastic properties with added moisture is caused by the disruption of some of the hydrogen bonds by water. Our results seem to be in agreement with this picture when we consider that the corrected compliances for water-softened films fall on a curve very similar in form to that used by Nissan. The fact that the corrected compliances of the glycerol-softened films also fall on this curve, when weighted by a constant factor, indicates that the glycerol actually is acting in the same way as the water which, in terms of Nissan's view, means that they are both bringing about a softening of the cellulose structure by breaking some of the hydrogen bonds between cellulose chains. The factor 2 applied to the number of moles of glycerol may be taken to mean, therefore, that a molecule of glycerol is capable of breaking twice as many hydrogen bonds as is a molecule of water. It is also significant that the results obtained on the ethylene carbonate and ethylenediamine films fall on the same curve with the single exception of the ethylenediamine films tested at high humidity. These other materials

also seem to be acting on the cellulose in the same way as water.

On the basis of these experiments, therefore, we feel that the point of view that softening action results from partial disruption of the hydrogen-bonded structure of cellulose has been reaffirmed and that methods have been developed for obtaining a quantitative measure of the relative effects of added materials on the elastic modulus of regenerated cellulose.

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Synopsis

The dynamic elastic modulus of cellophanes has been measured by use of the resonant frequency of a 2×60-mm. strip of film in longitudinal vibration. The modulus was computed from the resonant frequency length of specimen, and the cross-sectional area determined from its resonant frequency in transverse vibration. The apparatus is described briefly. Unsoftened film and glycerol-softened films containing 7.3, 13.7, and 21.3% glycerol prepared from the same roll of never-dried regenerated cellulose were conditioned at 75°F. and 15, 35, and 81% R. H., and the elastic moduli were measured in both directions. Moisture and softener contents were determined. The reciprocals of the geometric means of the moduli in the machine and transverse directions were plotted as a function of the volume of film containing 1 g. of cellulose. The displacement of the curve obtained for each softened film from the curve for the unsoftened film measures the effect of the softener, since the curves would coincide if the effect of softener were from swelling only. This permits construction of an empirical equation for the modulus of these glycerol-softened films as a function of moisture and softener content. It was found further that the logarithms of the corrected compliance $(1/EV_c{}^{2/3})$, where E is the geometric mean modulus and V_c is the volume of film containing 1 g. of cellulose, gave a straight line when plotted as a function of the number of moles of water plus twice the number of glycerol present in 100 g. of cellulose. This indicates that the effect of a mole of glycerol in breaking up the hydrogen-bonded structure of the cellulose is twice as great as that of a mole of water. These results have been compared with similar results obtained on films containing ethylene carbonate and ethylenediamine. With the exception of ethylenediamine-treated films studied at high humidities, these films gave points falling approximately on the corrected compliance curve obtained for the glycerol-softened and unsoftened films. For these films, however, the simple sums of moles of water plus moles of ethylene carbonate or ethylenediamine monohydrate present in 100 g. of cellulose were used rather than the weighted sum used for the glycerol-softened films.

Résumé

On mesure le module d'élasticité dynamique des cellophanes au moyen de la fréquence de résonance d'une bande de film de 2×60 mm en vibration longitudinale. On calcule le module à partir de la longueur de fréquence de résonance de l'échantillon, et on détermine la surface de la section transversale à partir de cette fréquence de résonance en vibration transversale. On décrit brièvement l'appareillage. On conditionne, à 75°F et à 15, 35 et 81% d'humidité relative, un film non-traité et des films traités au glycérol contenant 7,3, 13,7, et 21,3% de glycérine, et préparés à partir du même rouleau de cellulose régénérée qui n'a jamais été séchée, et on mesure les modules d'élasticité dans les deux directions. On détermine le degré d'humidité et la teneur en émollient. On trace en fonction du volume de film contenant un gramme de cellulose, les valeurs inverses des moyennes géométriques des modules dans l'appareil et les directions transversales. Le déplacement de la courbe obtenue pour chaque film traité par rapport à celle du film non-traité mesure l'effet du plastifiant, puisque les courbes coincideraient si l'effet du plastifiant se réduisait uniquement à un gonflement. Ceci permet d'élaborer une équation empirique pour le module de ces films plastifiés à la glycérine en fonc-tion de l'humidité et de la teneur en plastifiant. On a trouvé ensuite que les logarithmes de la valeur corrigée de $(1/EV_c{}^{2/3})$, où E est la moyenne géométrique de module et V_c le volume de film contenant un gramme de cellulose, se placent sur une ligne droite en un diagramme en fonction du nombre de molécules d'eau plus deux fois le nombre de molécules de glycérine présent dans 100 gr de cellulose. Ceci indique que l'effet d'une môle de glycérine dans la rupture de la structure due aux liens-hydrogène de la cellulose est deux fois plus grand que celui provoqué par une môle d'eau. Ces résultats ont été comparés à des résultats similaires obtenus sur des films contenant du carbonate d'éthylène et de l'éthylènediamine. A l'exception de films traités à l'éthylènediamine, étudiés à hauts degrés d'humidité, les films donnent des points qui se situent approximativement sur la courbe corrigée obtenue par les films traités et non-traités avec de la glycérine. Pour ces films, cependant, la simple somme des môles d'eau et des môles de carbonate d'éthylène ou de monohydrate d'éthylènediamine présentes dans 100 gr de cellulose est utilisée de préférence à la somme en poids employée pour les films traités à la glycérine.

Zusammenfassung

Der dynamische Elastizitätsmodul von Cellophanproben wurde mittels der Resonanzfrequenz eines 2×60 mm Filmstreifens bei Longitudinalschwingung gemessen. Der Modul wurde aus der Resonanzfrequenzlänge der Probe berechnet und die Querschnittsfläche aus ihrer Resonanzfrequenz bei Transversalschwingung bestimmt. Die Apparatur wird kurz beschrieben. Nicht-weichgemachter Film und Filme mit 7,3, 13,7 und 21,3% Glycerin als Weichmacher die von derselben Rolle einer niegetrockneten, regenerierten Cellose hergestellt worden waren, wurden bei 75°F und 15, 35 und 81% relativer Feuchtigkeit konditioniert und der Elastizitätsmodul in beiden Richtungen gemessen. Feuchtigkeits- und Weichmachergehalt wurden bestimmt. Der Reziprok-wert des geometrischen Mittels der Moduli in der Beanspruchungs- und Transversalrichtung wurde als Funktion des einem Gramm Cellulose entsprechenden Filmvolumens aufgetragen. Die Verschiebung der für den weichgemachten Film erhaltenen Kurve gegen die Kurve des nicht weichgemachten Films ist ein Mass für die Wirkung des Weichmachers, da die Kurven bei blossem Quellungseinfluss des Weichmachers zusammenfallen würden. Dadurch wird die Aufstellung einer empirischen Gleichung für den Modul dieser glycerinweichgemachten Filme als Funktion des Feuchtigkeits- und Weichmachergehalts ermöglicht. Weiters wurde gefunden, dass der Logarithmus der korrigierten Nachgiebigkeit $(1/EV_c{}^{2/3})$, wo E das geometrische Mittel des Moduls und V_c das einem Gramm Cellulose entsprechende Filmvolumen ist, beim Auftragen als Funktion der Zahl der Mole Wasser plus der doppelten Zahl der Mole Glycerin in 100 g. Cellulose eine gerade Linie ergibt. Das läss erkennem, dass die Wirkung eines Mols Glycerin beim Aufbrechen der Wasserstoffbindungsstruktur der Cellulose doppelt so gross wie die eines Mols Wasser ist. Diese Ergebnisse wurden mit ähnlichen, an Äthylenkarbonat und Äthylendiamin enthaltenden Filmen verglichen. Mit Ausnahme der äthylendiamin-enthaltenden Filme bei hoher Feuchtigkeit lieferten diese Filme Punkte, die angenähert auf der für glycerin-weichgemachte und nicht-weichgemachte Filme erhaltenen Nachgiebigkeitskurve lagen. Bei diesen Filmen wurde aber einfach die Summe der Mole Wasser und Mole Äthylenkarbonat oder Äthylendiaminmonohydrat in 100 g. Cellulose anstatt der für die glycerinweichgemachten Filme benützten gewogenen Summe herangezogen.