

## Viscoelastic Properties of Regenerated Cellulose Sheet

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### INTRODUCTION

The durability properties of cellophane are measured at the present time by several physical tests, such as measurement of impact strength, flexing under stress, tenacity, elongation, tear, and others, and no correlation between these test data and the structure and interaction of the polymer chains exists. Several studies in our laboratories have indicated that there is little relation, if any, among the physical tests mentioned, and that therefore none of these tests when used separately is indicative of the performance of cellophane in use. To relate the performance of cellophane to its molecular structure we have attempted to evaluate the deformation of regenerated cellulose under stress in terms of a mechanical model and to correlate the elastic and viscous flow portions of this model with the interactions between cellulose chains in the absence and presence of various small molecules of different types and concentrations.

In previous investigations<sup>1,2</sup> we have studied the interaction between cellulose and various small molecules in terms of the relative affinity of cellulose and of the softener molecule for water. We have obtained some quantitative data relating the interaction of small molecules to their chemical nature and to their hygroscopic properties.

As a continuation of this investigation we have studied the effect of the added small molecules on the mechanical properties of cellophane. In particular, the behavior of the elastic modulus of cellophane, impregnated with several small molecules such as glycerol, ethylene carbonate, ethylenediamine, and with water only was studied and related to the softening process.<sup>3</sup>

In the present investigation we have studied the creep of cellophane in the presence of various small molecules. Curves relating strain to time were obtained and evaluated in terms of a simple mechanical model. The effect of the added molecules on the elastic and viscous parameters of the model was determined and compared with the

elastic modulus of the same films when measured separately.

The interpretation of our data in terms of cellulose-softener interaction shows good correlation with the work carried out on the dynamic tensile modulus instrument used for measuring elastic moduli.<sup>3</sup> It also agrees well with Nissan's interpretation of Young's modulus in terms of hydrogen bonding.<sup>4</sup> In addition, a relationship was found between the retarded elasticity and the interaction energy of the added softener molecules. This points to a new interpretation of cellulose-softener interaction in terms of hydrogen-bond energies.

### EXPERIMENTAL

#### Apparatus and Materials

All viscoelastic measurements reported here were made on a Model TTB Instron tensile tester using a type C load cell of range 1-50 lb. All measurements were made in air-conditioned laboratories at 75°F. and 35% R.H. To hold the film specimen, two jaws were used which had faces 3 in. wide in the rear, 1 in. wide in the front, and 1.5 in. in height. Thus the film specimens which were cut with a 3- × 6-in. template were held across a 1-in. center width at a 3-in. gage length. All determinations were made in the dimension transverse to the machine direction of manufacture.

The cellophane samples used in these experiments were prepared on our laboratory impregnator drier from gel film supplied by the Pisgah Forest plant. Films were prepared containing a variety of softeners\* at different softener and moisture content as shown in Table I; all data are expressed on a dry cellulose basis.

\* We here employ the term softener in a broad reading, not in the commercial sense. For convenience, we have called all added small molecules softeners, without concern for their commercial or practicable limitations.

TABLE I  
Preparation of Film Samples

Film no.	Softener	Concentration of softener, % <sup>a</sup>	Moisture, % <sup>a</sup>
CD-1B	Glycerol	20.0	6.8
CD-4	Glycerol	29.1	7.3
CD-8	Triethylene glycol	23.9	7.0
CD-11	Ethylenediamine	18.0	6.4
CD-12	Unsoftened film	0	9.1
CD-41	Glycerol	18.9	8.0
CD-43	Ethylene glycol	12.7	7.3
CD-44	Propylene glycol	12.5	7.4
CD-45	Diethylene glycol	15.9	7.7
CD-46	1,3-Butanediol	15.4	8.0
CD-47	Ethylene carbonate	15.1	7.0
CD-48	Unsoftened film	0	9.2
CD-52	Diethanolamine	14.6	9.6

<sup>a</sup> After conditioning at 75°F. and 35% R.H.

### Young's Modulus

Young's modulus of elasticity was determined for the first five softened and unsoftened films of Table I (CD-1B through CD-12) by simple stress-elongation measurements in the transverse direction. The Instron machine was operated at a crosshead speed of 1.2 in./min. and a chart speed of 20 in./min. Film specimens were elongated at constant rate to 0.33, 0.66, 1.00, and 1.30% deformation (preset on the Instron). The actual elongation and

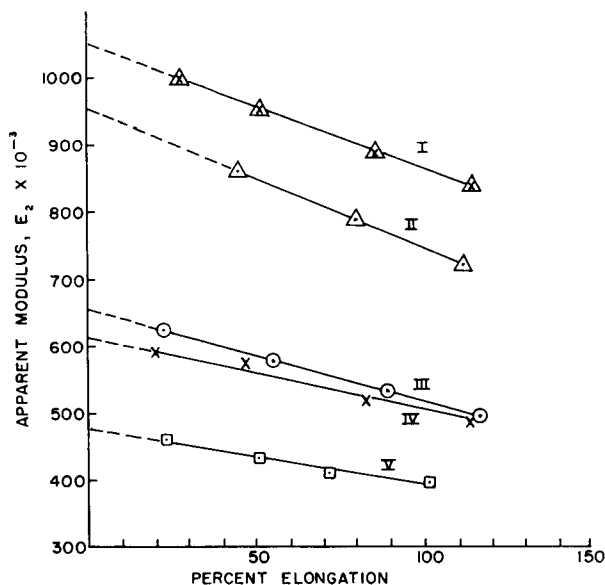


Fig. 1. Apparent Young's modulus as a function of elongation: (I) unsoftened film containing 9.1% water; (II) film with 18.0% ethylenediamine; (III) film with 20.0% glycerol; (IV) film with 23.9% triethylene glycol; (V) film with 29.1% glycerol.

TABLE II  
Apparent Young's Modulus at Various Elongations and Loads

Film no.	Softener	Instron setting, %	Extension, %	Modulus, (lb./in. <sup>2</sup> ) × 10 <sup>-3</sup>
CD-1B	Glycerol	0.33	0.23	625
		0.66	0.55	578
		1.00	0.89	535
CD-4	Glycerol	1.30	1.16	495
		0.33	0.23	463
		0.66	0.51	433
CD-8	Triethylene glycol	1.00	0.71	409
		1.30	1.01	398
		0.33	0.20	592
CD-11	Ethylenediamine	0.66	0.47	579
		1.00	0.82	521
		1.30	1.13	492
CD-12	Unsoftened film	0.33	0.18	748
		0.66	0.45	860
		1.00	0.80	816
CD-4	Glycerol	1.30	1.12	723
		0.33	0.28	1000
		0.66	0.51	952
CD-8	Triethylene glycol	1.00	0.86	888
		1.33	1.14	843

corresponding stress were read from the Instron, and the apparent modulus was then calculated by Hooke's Law for an assumed width of 1 in. and a constant thickness of 1 mil. Three different specimens of film were measured at each Instron setting, from which the average extension and modulus were calculated as shown in Table II. From the apparent moduli the real elastic moduli were obtained by plotting apparent moduli against elongation and extrapolating to zero elongation as

TABLE III  
Young's Modulus of Various Softened Films. Extrapolated Values

Film no.	Softener	Young's modulus	
		(lb./in. <sup>2</sup> ) × 10 <sup>3</sup>	(dynes/cm. <sup>2</sup> ) × 10 <sup>-10</sup>
CD-1B	Glycerol (20.0%)	655	4.52
CD-4	Glycerol (29.1%)	475	3.27
CD-8	Triethylene glycol (23.9%)	610	4.20
CD-11	Ethylenediamine (18.0%)	955	6.58
CD-12	Unsoftened film (9.1% H <sub>2</sub> O)	1050	7.24

shown in Figure 1. The real moduli are given in Table III.

The data show the effect of softener type and concentration on film stiffness. Glycerol and triethylene glycol are equivalent, while ethylenediamine makes cellophane almost as stiff as unsoftened film containing only moisture. A high glycerol concentration, on the other hand, results in a film of low modulus.

### Creep Curves

The creep and creep-recovery curves were obtained by use of the Instron tensile tester as follows. The film specimen was elongated at 1 in./min. to a load of 12.5 lb. The film was then allowed to relax until the load decayed to 12.25 lb., whereupon the film was again elongated at 1 in./min. to the upper limit of 12.5 lb. This cycling procedure was continued for 7 min. while the elongation was recorded from the Instron dials. The frequency of response is indicative of the rate of creep.

After creep had been measured over the 7-min. time interval, the Instron machine was switched to the lower load limit of 0.25 lb. (by changing to a 1-lb. load range) and the strain recovery was again recorded from the instrument.

TABLE IV  
Creep and Creep Recovery at Constant Load

Time, min.	CD-41	CD-48
	Glycerol-softened film deformation, in.	Unsoftened film deformation, in.
	Creep	
0	0.0750	0.0450
0.1	0.1200	0.0475
0.5	0.2000	0.0600
1	0.2250	0.0650
2	0.2550	0.0750
3	0.2850	0.0775
4	0.2950	0.0850
5	0.3075	0.0850
6	0.3150	0.0900
7	0.3250	0.0925
	Recovery	
0	0.2500	0.0475
0.5	0.2050	0.0375
1	0.1950	0.0325
2	0.1850	0.0275
3	0.1750	0.0275
4	0.1725	0.0250
5	0.1700	0.0250
6	0.1650	0.0225
7	0.1650	0.0225

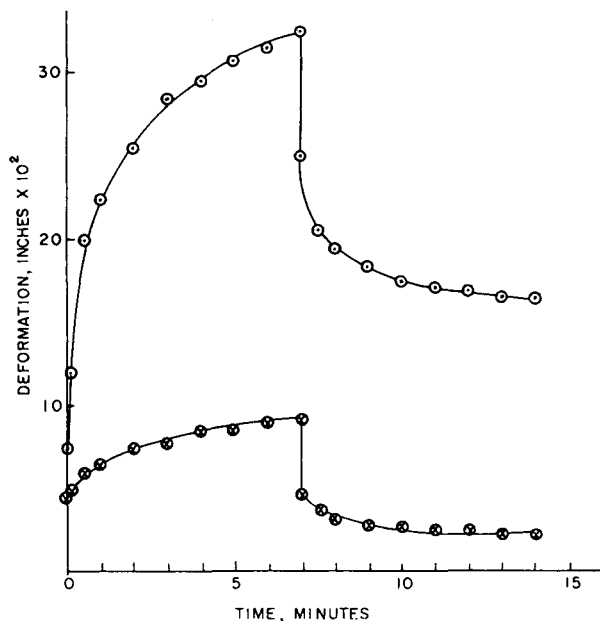


Fig. 2. Strain curves of unsoftened film (lower curve) and glycerol-softened film (18.9%, upper curve) as a function of time. Tensile stress was kept constant at  $12.5 \times 10^3$  lb./in.<sup>2</sup>.

Representative Instron data for a glycerol-softened and unsoftened film are given in Table IV, and the corresponding plots of strain as a function of time, made from these data, are shown in Figure 2. The elastic and inelastic deformation obtained for these and all other films tested have been summarized in Table V.

A simple mechanical model representing the elastic and viscous behavior of cellophane was fitted to these curves. Use of this model (Fig. 3) consisting of Maxwell and Voigt elements of springs and dashpots in series assumes linear viscoelastic behavior of cellophane, although we recognize that the behavior of cellophane is actually nonlinear. The assumption of linearity is made for simplicity. The experimental strain behavior of cellophane as a function of time has been represented by conditions in the model corresponding to certain times (Fig. 4).<sup>5</sup> The film specimens were subjected to a constant stress of 12.5 lb. at a time  $t_0$ . During step 1 for a time interval  $(t_1 - t_0)$ , we observe an immediate elastic deformation of the Maxwell spring (at time  $t_0$ ) corresponding to diagram (a) in Figure 4, followed by a slower extension of the Voigt element, diagram (b); finally the Maxwell dashpot begins to move, corresponding to inelastic deformation, also shown in diagram (b). In step 2, the film is quickly returned to zero load at time  $t_1$ . The Maxwell spring immediately returns

TABLE V  
Elastic and Inelastic Deformation of Softened and Unsoftened Films under 12.5 lb./in.<sup>2</sup> Load

Film no.	Softener	Water, %	Deformation, in.		
			Elastic	Recoverable	Unrecoverable
CD-41	Glycerol (18.9%)	8.0	0.0750	0.0850	0.1650
CD-43	Ethylene glycol (12.7%)	7.3	0.0502	0.0425	0.0500
CD-44	Propylene glycol (12.5%)	7.4	0.0550	0.0425	0.0550
CD-45	Diethylene glycol (15.9%)	7.7	0.0700	0.0600	0.1150
CD-46	1,3-Butanediol (15.4%)	8.0	0.0600	0.0400	0.0800
CD-47	Ethylene carbonate (15.1%)	7.0	0.0600	0.0375	0.0675
CD-52	Diethanolamine (14.6%)	9.6	0.0800	0.0800	0.1700
CD-48	Unsoftened film	9.2	0.0450	0.0250	0.0225

to zero extension as shown by diagram (c). Creep recovery occurs during step 3 over the permitted time interval ( $t_2 - t_1$ ), corresponding to the movement of the Voigt element to its original position as shown in (d). Only the nonrecoverable deformation of the Maxwell dashpot remains at this time.

### Viscoelastic Constants

To determine the parameters and constants for this model let us consider the following. The total deformation  $\gamma$  is equal to  $\gamma_1 + \gamma_2 + \gamma_3$ , where  $\gamma_1$

represents pure elastic deformation of the Maxwell spring only,  $\gamma_2$  is the retarded elastic deformation of the Voigt model only, and  $\gamma_3$  corresponds to the viscous deformation of the Maxwell dashpot.

The values of the parameters  $E_1$ ,  $E_2$ ,  $\eta_2$ , and  $\eta_3$  can then be calculated from the following relationships:

$$\gamma_1 = S/E_1 \quad (1)$$

$$\gamma_2 = (S/E_2)(1 - e^{-t/T_2}) \quad (2)$$

where

$$T_2 = \eta_2/E_2$$

$$\gamma_3 = (S/\eta_3)t \quad (3)$$

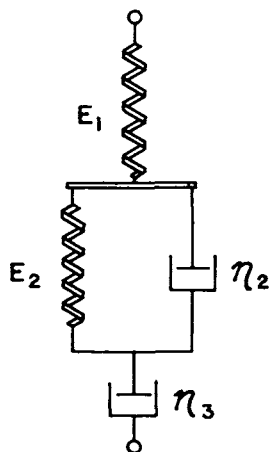


Fig. 3. Mechanical model representing the stress-strain relationship of cellophane. The upper elastic element of the Maxwell model represents elastic deformation and the lower Maxwell element represents unrecoverable creep. The interposed Voigt elements (spring and dashpot in parallel with each other) represent the recoverable creep.  $E_1$  and  $E_2$  are the spring constants and  $\eta_2$  and  $\eta_3$  are the dashpot viscosities.

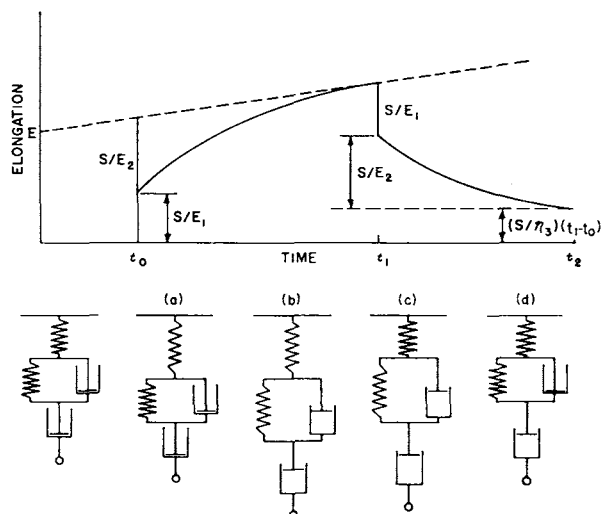


Fig. 4. Interpretation of strain-time relation at constant stress,  $S$ . The strain-time curve corresponds to the following conditions of the model: initial state; (a),  $t_0$ ; (b), just before  $t_1$ ; (c),  $t_1$ ; (d),  $t_2$ .

TABLE VI  
 Determination of Model Constants

Spring constant	$E_1 = S/\gamma_1$	Pure elastic deformation
Spring constant	$E_2 = (S/\gamma_2)_\infty$	
	$S = E_2\gamma_2 + \eta_2 d\gamma_2/dt$	
	(At $t_1$ , $\eta_2 d\gamma_2/dt = 0$ )	
Viscosity of dashpot (proportional to unrecoverable creep)	$\eta_3 = (S/\gamma_3)t$	$\gamma_3$ is the deformation owing to the viscous element only
Viscosity of dashpot, Voigt model (related to recoverable creep)	$\eta_2 = E_2 T_2$	$T_2$ is the retardation time obtained from $\ln \gamma_2 = \ln \gamma_2^0 - t/T_2$ , where $-1/T_2$ is slope of curve and $\gamma_2^0 = \gamma_2$ at $t_1$
Overall modulus	$E = \left(\frac{1}{E_1} + \frac{1}{E_2}\right)^{-1}$	Model in series
Total deformation at time $t$	$\gamma = \frac{S}{E_1} + \frac{S}{E_2} (1 - e^{-t/T_2}) + t \frac{S}{\eta_3}$	
	( $\gamma = \gamma_1 + \gamma_2 + \gamma_3$ )	

 TABLE VII  
 Parameters for Deformation-Time Curves at  $12.5 \times 10^3$  lb./in.<sup>2</sup> Tensile Stress

Softener <sup>a</sup>	$E_1 \times 10^{-5}$ , lb./in. <sup>2</sup>	$E_2 \times 10^{-5}$ , lb./in. <sup>2</sup>	$E \times 10^{-5}$ , lb./in. <sup>2</sup>	$\eta_2 \times 10^{-6}$ , lb.-min./in. <sup>2</sup>	$\eta_3 \times 10^{-6}$ , lb.-min./in. <sup>2</sup>
Glycerol (18.9%)	5.00	4.42	2.29	0.294	1.59
Ethylene glycol (12.7%)	7.50	8.82	4.07	0.585	5.25
Propylene glycol (12.5%)	6.83	8.82	3.85	0.585	4.78
1,3-Butanediol (15.4%)	6.25	9.38	3.74	0.734	3.24
Diethylene glycol (15.9%)	5.35	6.25	2.89	0.475	2.29
Diethanolamine (14.6%)	4.69	4.69	2.35	0.346	1.54
Ethylene carbonate (15.1%)	6.25	10.00	3.86	0.795	3.88
Unsoftened film (9.2 water)	8.35	15.00	5.37	1.47	11.65

<sup>a</sup> As per cent of the weight of cellulose.

Here the  $E$ 's represent the indicated spring constants,  $S$  is applied stress, and the  $\eta$ 's represent viscosities of the designated elements. Since the curves can be separated into the contributions  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$  as shown in Figure 4,  $E_1$  can be immediately determined from eq. (1) and  $\eta_3$  from eq. (3).

$E_2$  is determined from the extrapolated extension  $\gamma_2$  at infinite time;  $T_2$  can be determined from the slope of the plot of  $\log(1 - \gamma_2 E_2/S)$  as a function of time. Alternatively,  $T_2$  can also be obtained from the plot of  $\ln \gamma_2$  as a function of time in the creep recovery curve. The determination of the model constants is summarized in Table VI.

The model parameters were then calculated for the softened and unsoftened films by use of the data of Table V. The results are given in Table VII.

## DISCUSSION OF RESULTS

### Modulus of Elasticity

The elastic modulus was determined as described in the experimental section. If the logarithms of

these moduli (given in Table III) for glycerol-softened films and for the unsoftened film are plotted as a function of the total effective molar concentration<sup>3</sup> (the concentration multiplied by an appropriate weighting factor), it is found that the data fall on a straight line. The modulus data for other softeners also fit this line if their molar concentrations are weighted by suitable factors. Since, as has been described previously,<sup>3</sup> the abscissa of this curve is a function of the number of hydrogen bonds broken, the modulus may be considered a direct measure of softener effectiveness relative to water. These results are shown in Figure 5, and the effective molar concentrations of softener are given in Table VIII. The data include the films used in the creep measurements.

The factor weighting each softener with respect to water indicates that a mole of glycerol is twice as effective in interrupting hydrogen bonds as is a mole of water.<sup>3</sup> Although all of these other factors were arbitrarily assigned to each softener to secure fit to the glycerol-water curve, they agree with our experience regarding softener effectiveness on a

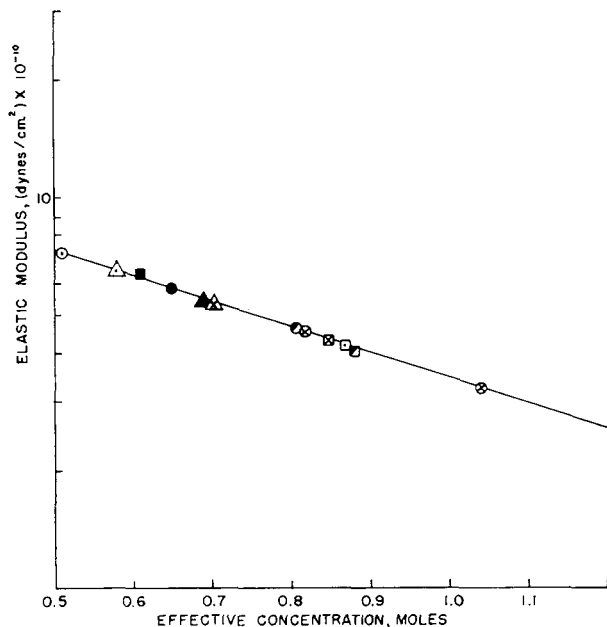


Fig. 5. Elastic modulus of cellophanes as a function of the effective molar concentration of softener. Beginning at the left, the points represent, respectively: water, ethylenediamine, ethylene glycol, propylene glycol, ethylene carbonate, 1,3-butanediol, diethylene glycol, glycerol (two points), triethylene glycol, diethanolamine, glycerol.

weight basis; i.e., three times as much softener is required by weight as water to produce durable cellophane at 35% R.H. Ethylenediamine is an exception, probably because of its strong complexing properties.<sup>6</sup>

Nissan has developed a theory of modulus for

TABLE VIII  
Effective Molar Concentrations of Softeners and Water

Softener	Softener concentration, moles	Factor	Water, moles	Effective concentration, moles
From Young's Modulus				
Water			0.51	0.51
Glycerol	0.22	2	0.38	0.82
Glycerol	0.32	2	0.40	1.04
Triethylene glycol	0.16	3	0.39	0.87
Ethylenediamine	0.30	0.75	0.36	0.58
From Mechanical Model				
Glycerol	0.20	2	0.44	0.84
Ethylene glycol	0.21	1	0.40	0.61
Propylene glycol	0.16	1.5	0.41	0.65
1,3-Butanediol	0.17	1.5	0.45	0.70
Diethylene glycol	0.15	2.5	0.43	0.81
Diethanolamine	0.14	2.5	0.53	0.88
Ethylene carbonate	0.17	1.75	0.39	0.69
Water			0.51	0.51

hydrogen-bonded solids.<sup>4</sup> In this theory the apparent modulus should decrease linearly with increasing strain for small strains, and the slope of the plot of apparent modulus as a function of strain should have a constant value of about  $1.0 \times 10^{12}$  dynes/cm.<sup>2</sup>. As can be seen from Figure 1, the modulus does decrease linearly with strain, and the average slope which would correspond to Nissan's constant  $K$  is calculated to be  $1.0 \pm 0.4 \times 10^{12}$  dynes/cm.<sup>2</sup>, in good agreement with Nissan's value.

### Creep Measurements

**a. Elastic Modulus.** Most of the work reported herein was done by making creep measurements using the Instron tensile tester and expressing the results in terms of the four-element model discussed above.

The modulus  $E_1$  was actually determined in a stress-elongation experiment. When measurements are made at a finite rate it is expected that this  $E_1$  should correspond to the Young's modulus of the material, also measured at the same finite rate. Since, however, the Young's moduli were effectively measured at zero strain, these values would be expected to be somewhat higher. If it is assumed that the ratio of moduli measured during the initial step of the creep experiments to the Young's moduli measured at zero is a constant (the former moduli correspond to the stress movement of a Maxwell element only), the  $E_1$  values can be adjusted to the same basis as the Young's moduli. When this was done, relative to the moduli of the water-softened films, it was found that all  $E_1$  values could be plotted on the same curve as the other modulus measurements as shown in Figure 5. The adjusted  $E_1$  values are given in Table IX.

**b. Viscous Flow.** In Figure 6 we have plotted log  $\eta_3$  as a function of log  $E_1$ . The linearity of this

TABLE IX  
Adjusted Elastic Moduli for Softened and Unsoftened Films<sup>a</sup>

Film no.	Softener	Elastic modulus, (dynes/cm.) $\times 10^{-10}$
CD-41	Glycerol	4.44
CD-43	Ethylene glycol	6.49
CD-44	Propylene glycol	5.92
CD-45	Diethylene glycol	4.63
CD-46	1,3-Butanediol	5.41
CD-47	Ethylene carbonate	5.44
CD-48	Unsoftened film	7.24
CD-52	Diethanolamine	4.08

<sup>a</sup> From creep experiments, Table VII.

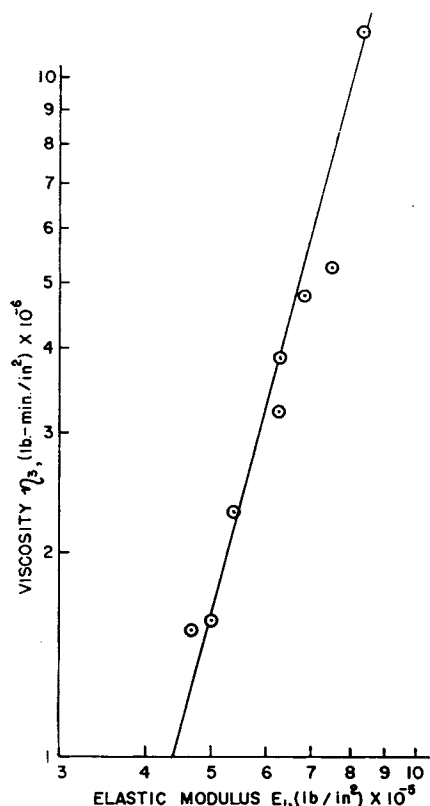


Fig. 6. Interdependence of the Maxwell parameters  $E_1$  and  $\eta_3$ .

plot indicates that  $\eta_3$  is functionally dependent on  $E_1$ . Therefore these properties are not independent and thus they depend on the effective molar concentration of softener in the same manner.

**c. Delayed Elasticity.** The delayed elasticity is a function of the amorphous structure of the system and represents short-range motion of chain segments. The activation energy of this movement is expected to be related to the difference between the internal energies of polymer and softener. If the free energy of the process is proportional to the difference in internal energy of the participants, we

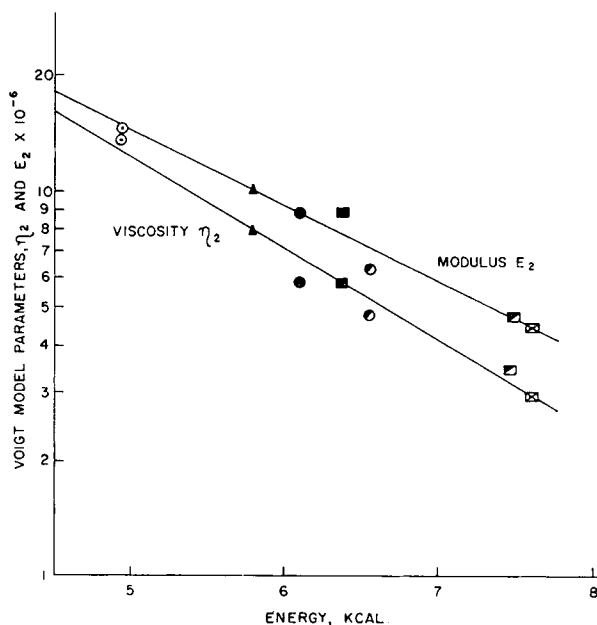


Fig. 7. Dependence of the Voigt model parameters  $E_2$  and  $\eta_2$  on the heat of vaporization of softener plus water present in the films; (⊠) glycerol; (■) ethylene glycol; (●) propylene glycol; (⊙) diethylene glycol; (▣) diethanolamine; (▲) ethylene carbonate; (○) water.

would expect that the logarithm of either the  $E_2$  modulus or the viscosity  $\eta_2$  should vary as a linear function of the heat of vaporization. When the logarithm of either  $E_2$  or  $\eta_2$  was plotted as a function of the energy (calculated by multiplying the number of moles of water by the heat of vaporization and adding the product of the number of moles of softener in 100 g. of cellulose and its heat of vaporization) a linear relationship was found (Fig. 7). The calculated energy values and the viscosities and moduli are given in Table X.

We know that for these particular softeners the heat of vaporization depends almost entirely on the energy necessary to break hydrogen bonds. We would suspect therefore that the deformation proc-

TABLE X  
Heat of Vaporization of Softeners (Including Water) in Regenerated Cellulose Sheets

Softener	Heat of vaporization, kcal.			$E_2 \times 10^{-5}$ , lb./in. <sup>2</sup>	$\eta_2 \times 10^{-6}$ , lb.-min./in. <sup>2</sup>
	Softener	Water	Total		
Glycerol	3.34	4.25	7.59	4.42	0.294
Ethylene glycol	2.48	3.88	6.36	8.82	0.585
Propylene glycol	2.12	3.98	6.10	8.82	0.585
Diethylene glycol	2.38	4.17	6.55	6.25	0.475
Diethanolamine	2.32	5.15	7.47	4.69	0.346
Ethylene carbonate	2.02	3.78	5.80	10.00	0.795
Unsoftened film		4.95	4.95	15.00	1.47

ess related to delayed elasticity requires breaking of interchain hydrogen bonds in contrast to the purely elastic deformation which involves the stretching of hydrogen bonds.

Both the moduli  $E_2$  and viscosities  $\eta_2$  decrease with increasing energy, indicating that the stronger the interaction between softener molecules the stronger is the interaction with cellulose; the cellulose-cellulose interaction is correspondingly weakened.

### CONCLUSION

It has been shown that at constant load the creep data for softened cellophanes can be fitted to a four-element model consisting of a Voigt unit and a Maxwell unit in series. The parameters of the Voigt model are closely related to each other, as are the parameters of the Maxwell model, but the two models seem to depend on the composition of the system in different ways.

The parameters of the Maxwell model depend on the total number of moles of softener added, i.e., on the number of cellulose interchain hydrogen bonds broken.

The parameters of the Voigt model, on the other hand, seem to depend on the internal pressure of the liquids carried by the cellulose. This is reflected in the sum of values for the heat of vaporization of the softeners (including water) and thus on the degree of interaction of these molecules with cellulose. A new interpretation of cellulose-softener interaction in terms of hydrogen bond energies is indicated; pure elasticity and plastic flow depend on stretching and finally on the breaking of hydrogen bonds, while delayed elasticity depends on the movement of polymer chain segments and requires breaking of interchain bonds.

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### Synopsis

The viscoelastic properties of regenerated cellulose containing several different softeners or water only were investigated. Measurements of creep and Young's modulus were made on the Instron tensile tester, and the creep curves were fitted to a mechanical model consisting of Voigt and Maxwell elements of springs and dashpots in series. The

elastic and viscous parameters were determined for the various softened films and compared with each other and with measurements of Young's modulus. It was found that the elastic modulus is a function of the effective molar concentration of the softener in the film which is related to its ability to break hydrogen bonds. The inelastic deformation was found to be a linear function of the heat of vaporization of softener (including water) in the film, which is related to hydrogen-bonding energy. Thus, inelastic deformation requires breaking of interchain hydrogen bonds in contrast to pure elastic deformation which involves stretching of hydrogen bonds. A relationship of the Voigt unit and of the Maxwell unit on the composition of the cellulose-softener system and on cellulose-softener interaction has been demonstrated.

### Résumé

On étudié les propriétés visco-élastiques de la cellulose régénérée contenant plusieurs plastifiants différents ou simplement de l'eau. Des mesures de rétrécissement et de module de Young ont été effectuées au moyen de l'appareil de mesures de tension Instron, et les courbes de rétrécissement ont été adaptées à un modèle mécanique consistant en des éléments de Voigt et Maxwell, ressorts et amortisseurs en série. On détermine les paramètres d'élasticité et de viscosité pour divers films traités et on les compare entr'eux et avec les mesures du module de Young. On trouve que le module d'élasticité est une fonction de la concentration molaire effective du plastifiant dans le film, qui est liée à son aptitude à briser les liaisons hydrogènes. On trouve que la déformation non-élastique est une fonction linéaire de la chaleur de vaporisation du plastifiant (l'eau y comprise) dans le film, laquelle est reliée à l'énergie de la liaison hydrogène. La déformation non-élastique demande donc la cassure des liens hydrogènes interchaines contrairement à la déformation élastique pure qui implique l'étirement des liaisons hydrogènes. On démontre qu'il existe une relation entre l'unité de Voigt et de Maxwell, la composition du système cellulose-plastifiant et l'interaction cellulose-plastifiant.

### Zusammenfassung

Die viskoelastischen Eigenschaften von regenerierter Cellulose, die verschiedene Weichmacher oder nur Wasser enthielt, wurden untersucht. Messungen des Kriechens und des Elastizitätsmoduls wurden mit dem Instron-Spannungsmesser durchgeführt und die Kriechkurven mit einem mechanischen Modell, das aus Voigt und Maxwell'schen Feder- und Reibungselementen in Serie besteht, wiedergegeben. Die Elastizitäts- und Viskositätsparameter wurden für die verschiedenen weichgemachten Filme bestimmt und untereinander und mit Messungen des Elastizitätsmoduls verglichen. Es wurde gefunden, dass der Elastizitätsmodul eine Funktion der effektiven molaren Konzentration des Weichmachers in dem Film ist, die in Beziehung zu seiner Fähigkeit, Wasserstoffbindungen zu spalten, steht. Die nichtelastische Deformation ist eine lineare Funktion der Verdampfungswärme des Weichmachers (einschliesslich Wasser) im Film, welche in Beziehung zur Wasserstoffbindungsenergie steht. Zu einer nichtelastischen Deformation ist die Spaltung von Wasserstoffbindungen zwischen den Ketten erforderlich, während eine rein elastische Deformation eine Dehnung der Wasserstoffbindungen mit sich bringt. Eine Beziehung der Voigt- und Maxwell-Einheit zur Zusammensetzung des Cellulose-Weichmacher-Systems und zur Wechselwirkung Cellulose-Weichmacher wurde gezeigt.