The Mechanism of Film Formation From Viscose

M. Miller and V. C. Haskell

Film Department, Cellophane Research and Development Laboratory, E. I. du Pont de Nemours & Company, Inc., Richmond, Virginia

Introduction

In a regenerated cellulose film a combination of properties, such as toughness, durability, and good dimensional stability, is desired. The base sheet must also serve the role of a strongly adhering support for coatings which contribute moistureproofness, heat-sealing properties, and desirable surface characteristics to the film. Since the property requirements of a cellulosic film are markedly different from those of a cellulosic fiber, one expects, and indeed finds, that different cellulosic fine structures will yield optimum properties. For example, the optimum structure in a cellulosic fiber is one of high orientation and low order. In contrast, the cellulosic film needs low order and low orientation. This paper relates the details of the process by which the film is formed to the film's mechanical properties through correlation of process with structure and structure with properties. The effect of the degree of polymerization, molecular orientation, and the degree of lateral order or crystallinity on the mechanical properties of a regenerated cellulose film will be discussed.

Molecular Weight

The dependence of the mechanical properties of a high polymer upon chain length is, qualitatively, the same for all systems; namely, a polymer of low degree of polymerization ($\overline{DP}$) is extremely weak, and as the $\overline{DP}$ increases the mechanical strength increases. For example, in a polymer of relatively low $\overline{DP}$, neighboring chains can slip past one another so that the sample breaks without the rupture of the chain molecules. With a very high $\overline{DP}$ this type of failure would require that long sections of molecular chains slide past one another and, consequently, the limiting strength of the polymer is determined by the chemical bond strength. Numerous experiments by various investigators have demonstrated that this phenomenon is valid for the cellulose polymer. The data presented in

Figure 1 show the effect of cellulose $\overline{DP}$ on some of the physical properties of cellophane that was prepared in our laboratory. These films were cast from viscose containing 9.0% cellulose and 5.5% sodium hydroxide by spreading a thin layer of viscose on a glass plate and then coagulating and regenerating the film under conditions normally used to produce commercial cellophane.[1] The softener content and the thickness of these films were maintained at constant values during these experiments. The slope and shape of these curves can be varied by changing the coagulating and regenerating conditions and the composition of the viscose.
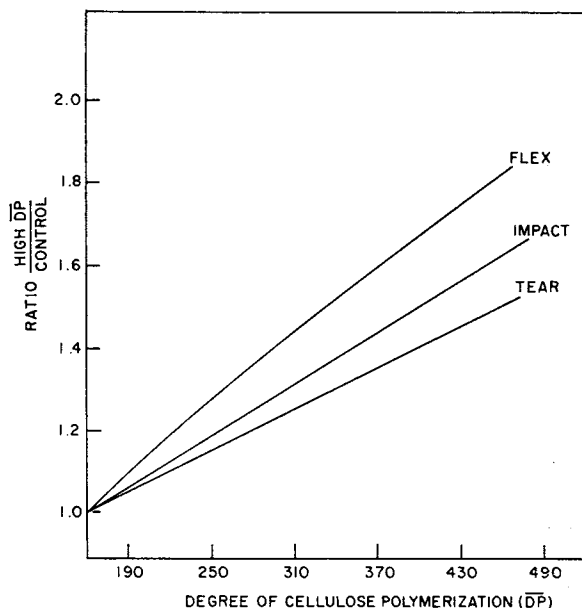

Fig. 1. Effect of cellulose $\overline{DP}$ on film properties.

Lateral Order

The degree of lateral order of the cellulose has a pronounced effect on the physical properties of a film.[2] Two examples are known of experimental

TABLE I
Fine Structure and Properties of Cellulose Films

Film type	Acid hydrolysis		X-ray diffraction, %	Tear, g.	Pendulum impact, kg.-cm.	Stress-flex, cycles
	Residue, %	L.O. DP	lateral order			
Regular	81.8	32	67	2.6	4.8	6.2
Dry-cast	70.0	20	20	25.6	18+	26
Deacetylated	65.0	19	15	12.0	18+	20

cellulosic films which have unusual toughness and extensibility even without a plasticizer being present. These are a film made by the deacetylation of cellulose acetate film in a nonaqueous system and a film made by dry-casting viscose and regenerating the dried film in a nonaqueous system. The dry-casting process is described in detail by Price and Haskell.[3] The data in Table I show the properties of these films compared with a conventionally prepared film from viscose and values which express the degree of lateral order of these structures. These data (x-ray diffraction, acid hydrolysis, and caustic swelling) point to a considerably lower order in the more durable films (dry-cast and deacetylated cellulose acetate).

Orientation in Films

Regenerated cellulose, when first formed, is usually in a highly swollen condition. Shrinkage in volume takes place upon dehydration and, concurrently, orientation is produced. The type of orientation is governed by the direction of shrinkage and the amount of orientation by the magnitude of this shrinkage.[4] Similarly, deformation or elongation produces orientation in a sample.

Cellulosic films were prepared, stretched and processed in the laboratory so that varying amounts of planar and axial orientation were present in the films. The definitions of types of orientation are those of Heffelfinger and Burton.[5] X-ray studies confirmed that the expected relative differences did exist in the samples. The stress–strain data presented in Figure 2 were obtained to define the effect that these changes in fine structure of the cellulosic sheet had on the mechanical behavior of the film. The data show that the tenacity parallel (machine direction, designated M.D.) to the direction of stretch (high axial orientation) was increased as the orientation was increased. Simultaneously,
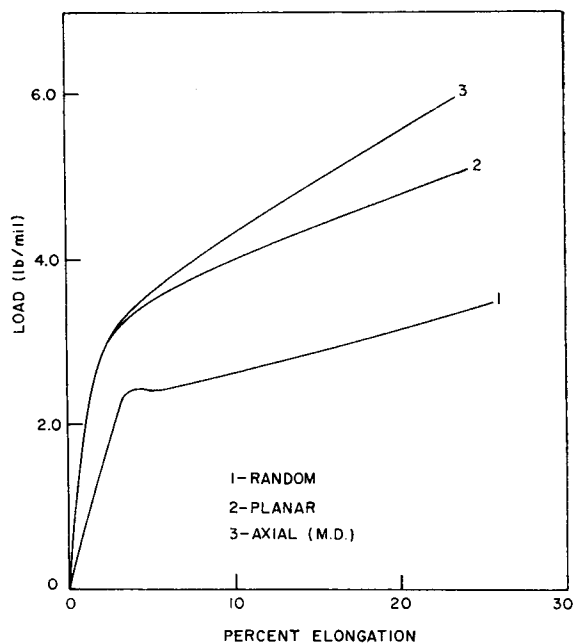

Fig. 2. Load–elongation behavior of films with different orientation (M.D. loading).

the elongation perpendicular (transverse direction, designated T.D.) to the direction of stretch was increased. The sequence of the curves is reversed when the direction of testing is changed from M.D. to T.D.

The data in Figures 3 and 4 show that, in general, imposing a mechanical stress caused an unbalance in the sheet by decreasing the elongation and in-
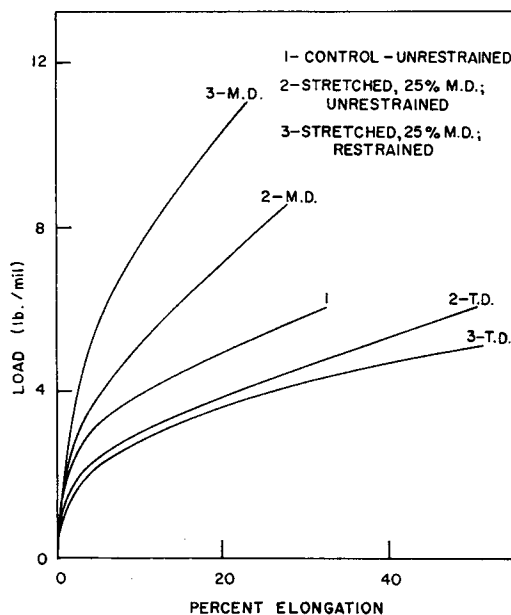

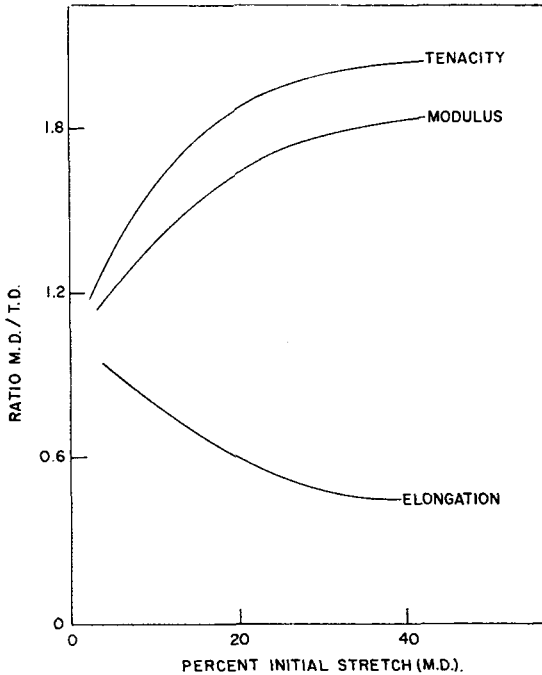Fig. 3. Load–elongation behavior of one-way stretched film.

regenerating conditions, can change the magnitude and shape of these curves.

One adverse consequence of machine direction stretching during sheet formation is that anisotropic properties are produced. The property levels in the machine and transverse directions vary with the amount of optical anisotropy as shown in Figure 5. It is seen that properties are improved in one direction and degraded in the other direction without much change in the average value. The net effect of the extra stretching during coagulation is harmful, since the film tends to fail in its weakest direction.

Coagulating and Regenerating Requirements

The degree of gel swelling, or the ratio of wet weight of cellulose to the dry weight of cellulose, of the film before final drying has been found to have an important effect on properties. Experimental films which are unusually tough are found to have low swelling in gel form. For example, the dry cast and deacetylated cellulose acetate films have gel swellings of about 2 whereas conventionally cast cellophane has a gel swelling of about 4. The low degree of swelling, while necessary for maximum toughness, is not a sufficient requirement for best properties. Numerous data show that the collapse leading to low swelling must be accomplished while the cellulose chains are well substituted; for example, with xanthate

Fig. 4. Effect of unidirectional stress on film properties.

creasing the tenacity and modulus in the direction of the applied stress. The amount of imbalance (ratio of M.D./T.D. properties) that resulted in a film was directly related to the amount of unidirectional stress that was imposed on the sample. Other process variables, such as the coagulating and
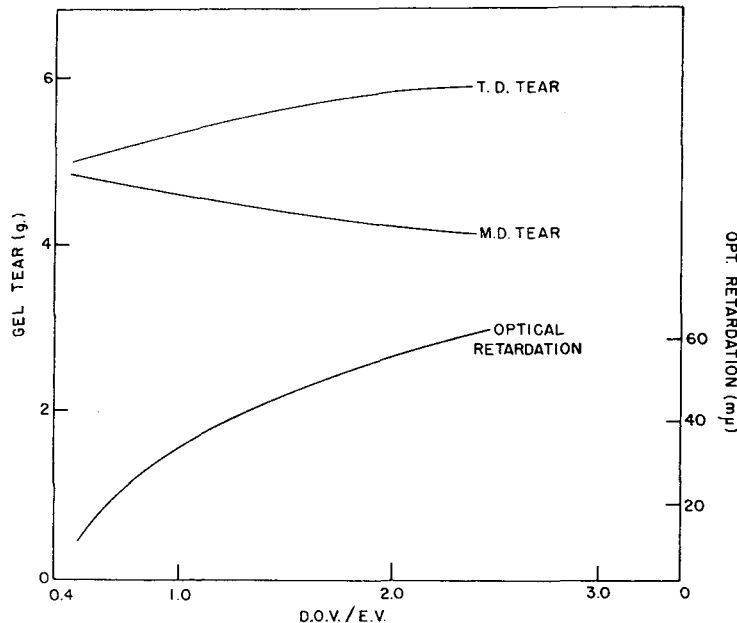

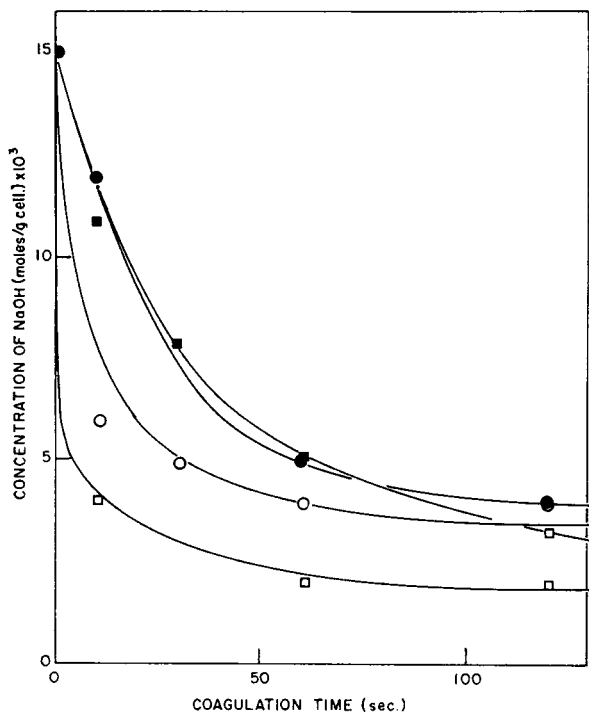Fig. 5. Dependence of gel tear and optical retardation on stretch during coagulation.

Fig. 6. Effect of degree of xanthation on loss of sodium hydroxide: (○) high xanthate viscose, cast in 45°C., 40% (NH₄)₂SO₄; (□) regular viscose, cast in 45°C., 40% (NH₄)₂-SO₄; (●) high xanthate viscose, cast in 45°C., 30% Na₂SO₄; (■) regular viscose, cast in 45°C., 30% Na₂SO₄.

groups or with acetate groups. Consequently sheet formation should occur in two discrete steps; the first step is the concentration of the solution of substituted cellulose to the maximum possible degree, and the second step is the removal of the substituent from the cellulose under conditions which minimize reswelling. The accomplishment of these steps under practical and economical conditions, as needed in the commercial production of cellophane, is a challenging problem.

At first it would seem that the techniques that have been developed for producing rayon tire cord would apply to the film process. However, there are at least two major problems in this approach. First, film formation requires a rapid coagulation process since, in order to maintain film area and avoid a wrinkled appearance, the film must be coagulated as close to the hopper as possible. The zinc baths with coagulation modifiers used in the rayon process are, generally, too slow for this purpose. Second, film transparency is one of the most important qualities of cellophane, and it has been found that many modified viscose systems do not yield clear films. Therefore, it is necessary to consider in more detail the viscose composition and

coagulating bath variables with special emphasis on the rates of the key steps leading to film formation. An approach based on the data presented would be to use a more highly substituted viscose than that normally used for cellophane and to select a bath which would dehydrate the viscose extensively prior to xanthate decomposition. Experiments with a viscose "enriched" in carbon disulfide in which there are used, in sequence, 40% ammonium sulfate as the coagulating bath and a conventional sulfuric acid–sodium sulfate bath for regeneration have given films with up to 200% improvement in physical properties.

The rates of dehydration and caustic removal with various viscoses and coagulating baths were studied in order to elucidate the mechanism through which this superior film structure was obtained. The technique used involved doctoring a known quantity of viscose onto a glass plate and then processing the viscose under various coagulating-regenerating conditions. The films were analyzed for residual alkali and their loss of water.
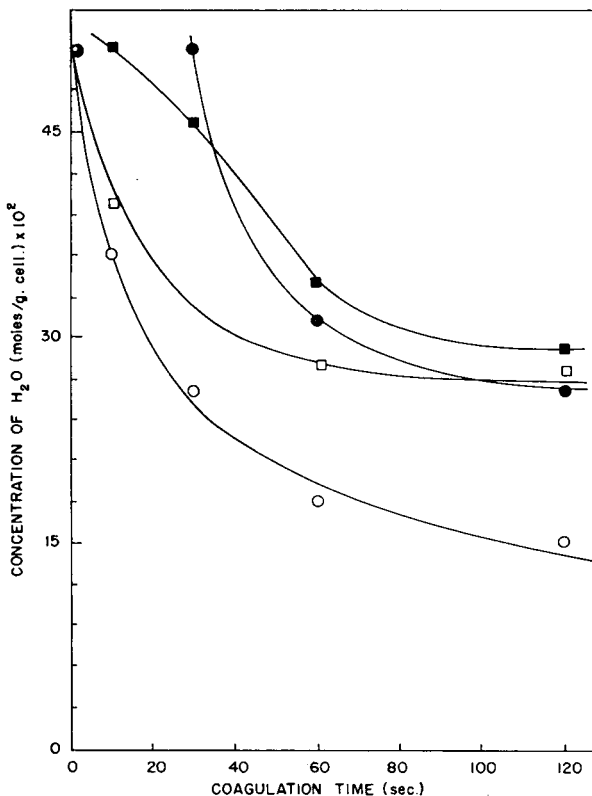

Fig. 7. Effect of degree of xanthation on loss of water: (○) high xanthate viscose, cast in 45°C., 40% (NH₄)₂SO₄; (□) regular viscose, cast in 45°C., 40% NH₄)₂SO₄; (●) high xanthate viscose, cast in 45°C., 30% Na₂SO₄; (■) regular viscose, cast in 45°C., 30% Na₂SO₄.
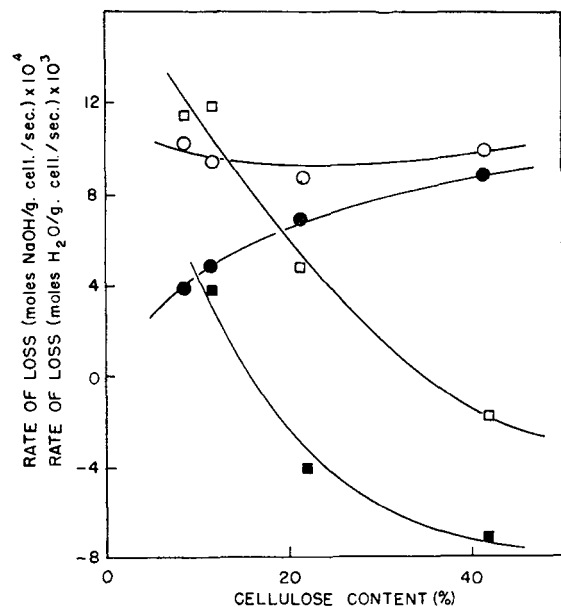
Fig. 8. Effect of cellulose content on rate of NaOH and H₂O loss: (O) 45°C., 40% (NH₄)₂SO₄ (NaOH); (●) 45°C., 30% Na₂SO₄ (NaOH); (□) 45°C., 40% (NH₄)₂SO₄; (H₂O); (■) 45°C., 30% Na₂SO₄ (H₂O).

Fig. 10. Effect of bath temperature on rate of NaOH and H₂O loss: (O) 40% (NH₄)₂SO₄ (NaOH); (●) sat. Na₂SO₄ (NaOH); (□) 40% (NH₄)₂SO₄ (H₂O); (■) sat. Na₂SO₄ (H₂O).
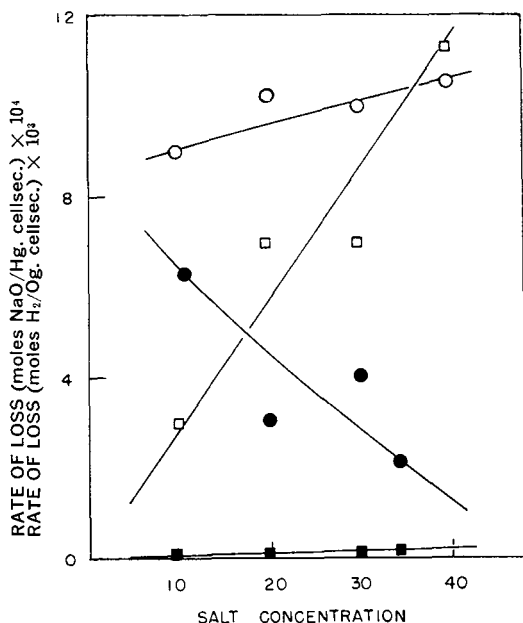

Fig. 9. Effect of bath concentration on rate of NaOH and H₂O loss: (O) 45°C., (NH₄)₂SO₄ (NaOH); (●) 45°C., Na₂SO₄ (NaOH); (□) 45°C., (NH₄)₂SO₄ (H₂O); (■) 45°C., Na₂SO₄ (H₂O).

The data presented in Figure 6 show that the rate of loss of sodium hydroxide was influenced by the degree of substitution of the sodium cellul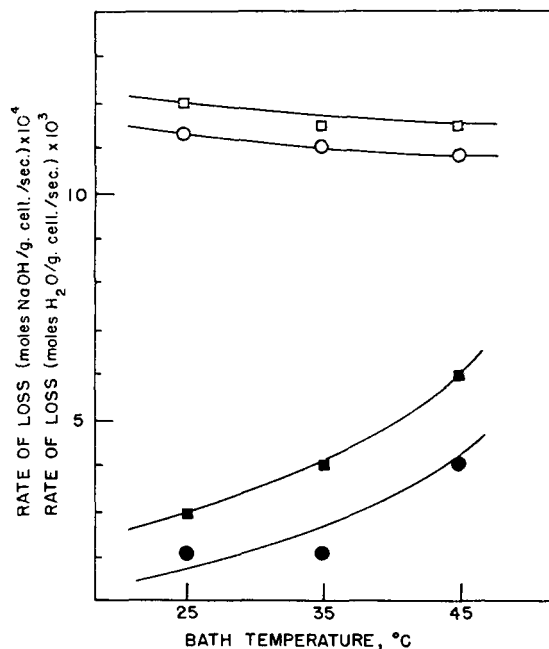ose xanthate. When cast in the same bath system, the more highly xanthated material retained more alkali than did the material that was less substituted. The rate of removal of the sodium hydroxide was faster in the ammonium sulfate bath. This behavior in the ammonium sulfate bath resulted because of the buffering and neutralizing action which is described later. From the data shown in Figure 7 we see that the more highly xanthated material retained less water than the less substituted material. In other words, the more highly xanthated material was associated with more sodium ions and remained in solution longer.

The effect of cellulose content on the rate of water loss is shown in Figure 8. The rate of water loss was most rapid with viscoses of low cellulose content; however, the extent of water removal was greatest with viscose of high cellulose content. It will be noted that the film prepared from the viscose of highest cellulose content actually became more hydrated during coagulation, since the affinity of the viscose for water exceeded that of the salt solution.

The cellulose content of the viscose had very little effect on the rate of sodium hydroxide removal. An increase in the cellulose content of the viscose was subsequently shown to decrease the penetration rate of the acid on a viscose basis but had little
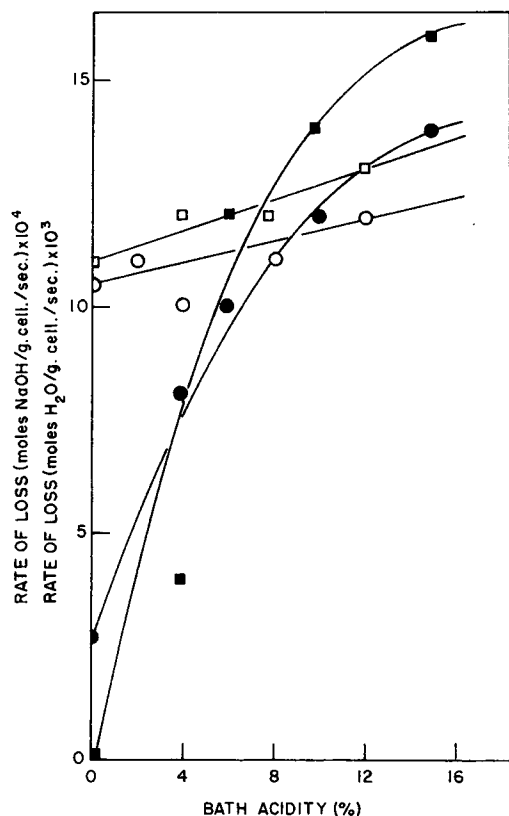
Fig. 11. Effect of bath acidity on rate of NaOH and H_2O loss: (O) 45°C., 40% $(NH_4)_2SO_4$ (NaOH); (●) 45°C., 18% Na_2SO_4 (NaOH); (□) 45°C., 40% $(NH_4)_2SO_4$; (H_2O); (■) 45°C., 18% Na_2SO_4 (H_2O).

effect on the rate of penetration on a dry cellulose basis.

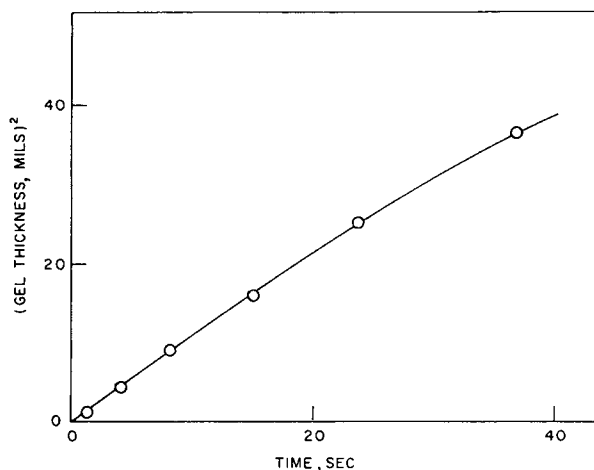The data presented in Figures 9 and 10 show the influence of changes in the concentration and tem-

Fig. 12. Rate of acid penetration through viscose film.

perature of the bath on the rates of loss of sodium hydroxide and water from the viscose. From these data it is seen that an increase in the salt concentration of a neutral bath, such as sodium sulfate, had minor effects on the rates of loss of water and sodium hydroxide from the viscose. It should be noted that, at the high concentrations of salt, the loss of sodium hydroxide was decreased as the concentration of the sodium sulfate was increased. In the case of a buffering and neutralizing bath such as ammonium sulfate, an increase in the salt concentration led to an increase in the rate of removal of sodium hydroxide and in the rate of removal of water from the viscose. The data also demonstrate that increases in temperature had minor effects on coagulation with a buffering and neutralizing bath. However, in the
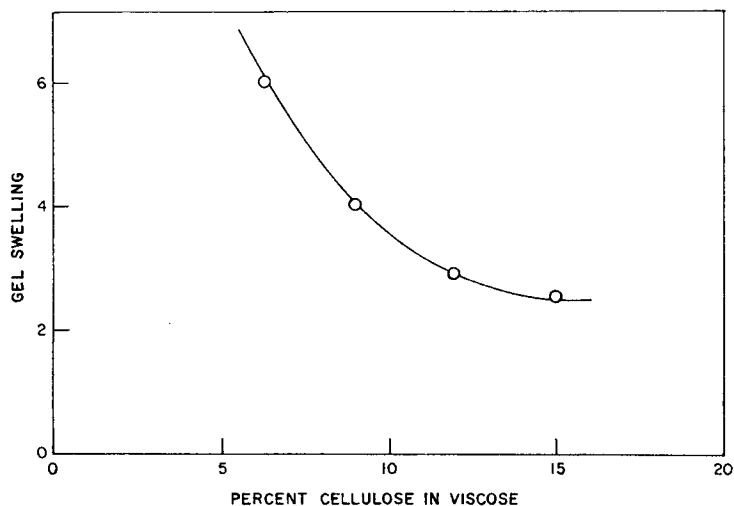

Fig. 13. Gel swelling as a function of viscose concentration.

case of a neutral bath, such as the sodium sulfate bath, the rates of removal of both sodium hydroxide and water was increased as the bath temperature was increased. These data were interpreted as showing that thermal and osmotic effects were not as important in determining the rate of coagulation as was the buffering and neutralizing capacity of the bath.

The effect of the addition of sulfuric acid to the coagulating bath is shown in Figure 11. Acidifying the bath caused an increase in the rate of removal and in the extent of removal of the sodium hydroxide, but with a buffering bath such as ammonium sulfate the effect was minimized. The high acid content caused regeneration prior to complete collapse of the film, and this resulted in films with high gel swelling when sulfuric acid was used in the coagulating bath.

The rate of acid penetration into a viscose film was studied by applying a uniformly tapered layer of viscose containing 0.2% bromcresol purple to a glass plate. The movement of the indicator boundary was converted to thickness penetrated by acid and was plotted as a function of time. This curve (Fig. 12) showed that the distance penetrated was proportional to the square root of the time. Conversely, the time required for penetration by the acid was proportional to the square of the depth penetrated.

From these data a comparison may be made of the rate of water loss and the rate of acid penetration if the assumption is made that the gel through which acid has passed has a uniform degree of swelling. By so doing it is possible to ascertain that there is little, if any, dehydration of the viscose at a site inside the film until acid has reached it when unmodified acid–salt bath is used. Continued exposure after complete penetration by acid produces continued dehydration but this part of the deswelling is reversible and reswelling occurs during washing with water.

Increasing the solids content of viscose generally improved the physical properties of the cellulosic film. Structurally, as shown in Figure 13, the increased cellulose content manifests itself in decreased gel swelling. Since the gel swelling is lower, reduced uniplanar orientation results, and this leads to the improvement in physical properties that is observed.

Summary

It has been demonstrated that the best mechanical properties of regenerated cellulose films are obtained when the cellulose has a high molecular weight, low lateral order, and low molecular orientation. The best way to achieve the highly condensed, disorganized structure necessary for maximum toughness is through the utilization of a high solids viscose with the cellulose highly enough substituted to permit extensive dehydration before regeneration is completed. Sheet formation should occur in two discrete steps; first, web collapse and, second, regeneration in a nonswelling system. Numerous variations in cellulose fine structure can be achieved by varying viscose composition and processing conditions. In the commercial production of cellophane, optimum conditions are sought within the limitations imposed by machine operability and process economics.

References

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Synopsis

The coagulating and regenerating conditions that are necessary for the formation of a highly durable cellulosic film are described. It is shown that low orientation, low lateral order, low gel swelling, and cellulose with a high $\overline{DP}$ are primary requisites for best film properties. Experiments demonstrated that the application of a unidirectional stress produced an unbalance of physical properties in the film, and this, in general, had an adverse effect on the durability level of a packaging film. Studies of the rates of loss of water and sodium hydroxide from the viscose during coagulation revealed that thermal and osmotic effects were not as important in determining the rate of coagulation as was the buffering and neutralizing capacity of the bath. A bath with high acid content caused the cellulose to be regenerated prior to collapse of the sheet.

Résumé

On décrit les conditions de coagulation et de régénération nécessaires pour la formation d'un film de cellulose très résistant. Les principales propriétés des meilleurs films sont: une faible orientation, un arragement latéral peu prononcé, un gonflement en gel peu prononcé et une cellulose de haut degré de polymérisation. L'expérience nous a

montré que l explication d'une force unidirectionnelle fournit des pellicules caractérisées par des propriétés physiques irrégulières, ce qui produit en général un effet opposé sur le niveau de résistance d'un film d'enballage. L'étude de la vitesse de perte en eau et en hydroxyde de soude de la viscose pendant la coagulation indique que les effets thermiques et osmotiques sont moins importants lors de la détermination de la vitesse de coagulation que la capacité de tampon et de neutralisation du bain. La synérèse joue un role important dans le phénomène de coagulation; un bain d'une teneur élevée en acide régénère la cellulose plutôt qu'il ne décompose la pellicule.

Zusammenfassung

Die für die Bildung eines gut haltbaren Cellulosefilms notwendigen Koagulierungs- und Regenerierungsbedin-gungen werden beschrieben. Es wird gezeigt, dass geringe Orientierung, geringe seitliche Ordnung, niedrige Gelquellung und Cellulose mit hohem $\overline{DP}$ die primären Erfordernisse für die besten Filmeigenschaften sind. Versuche zeigten, dass die Anwendung einer einseitig gerichteten Spannung un-gleichmässige physikalische Eigenschaften im Film erzeugt, wodurch im allgemeinen die Haltbarkeit eines Verpackungs-filmes nachträglich beeinflusst wird. Untersuchung des Wasser- und Natriumhydroxydverlustes der Viskose währ-end der Koagulation liess erkennen, dass thermische und osmotische Effekte nicht eine solche Bedeutung für die Grösse der Koagulationsgeschwindigkeit besassen, wie die Pufferungs- und Neutralisierungskapazität des Bades. Synärese spielt beim Koagulationsphänomen eine wichtige Rolle und ein Bad mit hohem Säuregehalt bringt die Cellu-lose vor dem Zusammenbruch der Folie zur Regenerierung.