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The Dry Casting of Viscose Film

C. R. PRICE and V. C. HASKELL

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

Introduction

Regenerated cellulose film, as obtained by the well known acid-regeneration process, has achieved outstanding commercial success. However, the trade has long recognized the need for a regenerated cellulose sheet characterized by high tear resistance, uniformity in all directions, toughness under cold, dry conditions even in the absence of softener, and good anchorage for moistureproof coatings. Early fundamental studies of fine structure by Nichols[1,2] of the Central Research Department of E. I. du Pont de Nemours and Co., Inc. provided the basis for a process by which viscose could be dry cast to form a transparent, regenerated cellulose film with outstanding physical properties. Other investigators have extended this work. The purpose of this article is to describe the dry-casting process, factors influencing the properties of film produced in this manner, and the structural features which contribute to the superior properties of this film.

The Dry-Casting Process

The process by which regenerated cellulose film may be produced by the dry-cast method can be summarized into three major steps. In Figure 1 a process suitable for commercialization of the viscose dry casting method is shown. It should be pointed out that the optimum viscose composition for the dry-cast process is considerably different from that desired for the conventional casting process. A detailed discussion of this factor will be made in a later section of this review.

The first major step in the dry-cast process is the extrusion of viscose in a film onto a heated, polished surface. This supporting surface may be in the form of a belt, plate, or rotating cylinder as shown in Figure 1. The purpose of this step of the process is to reduce the water content of the viscose to at least 45 wt.-%, preferably to 20%, before irreversible gelation takes place. The viscose drying step should be so closely controlled as to minimize any decomposition of the xanthate on the casting surface. The casting surface is enclosed in a shroud which allows the controlled flow of heated air over the viscose film.

The relatively large size of the xanthate groups in the viscose is of paramount importance at this stage of the process. Since the bulky xanthate groups tend to inhibit molecular interaction, they contribute considerably to the random structure so desirable in regenerated cellulose film.

The drying rate of the viscose will depend upon the temperature and velocity of air flowing past the supporting surface, as well as a number of other factors. The temperature of the air should be maintained high enough to reduce the humidity of the moving air to a practical minimum. The function of the moving air stream is to carry away the moisture as it becomes available at the film surface and to reduce the thickness of the stagnant vapor layer at the immediate film surface.

The temperature of the casting surface should be maintained at a maximum without causing boiling of the viscose. The film should be allowed to dwell on the supporting surface until the desired degree of concentration, previously mentioned, has been achieved, but the film should be stripped from the surface before it becomes brittle. The relationship between drying time and film thickness is illustrated in Figure 2. The line representing viscose containing 7% cellulose and 6% caustic shows that the drying time increases as a squared value as the thickness is doubled; a fact which indicates a diffusion-controlled drying process. However, the lower curve indicates that the variation in drying time is less pronounced for viscose containing 12% cellulose, but that the total drying time is less for viscose containing the higher concentration of cellulose.

The second major step in the process is regeneration of the viscose film. Regeneration may be

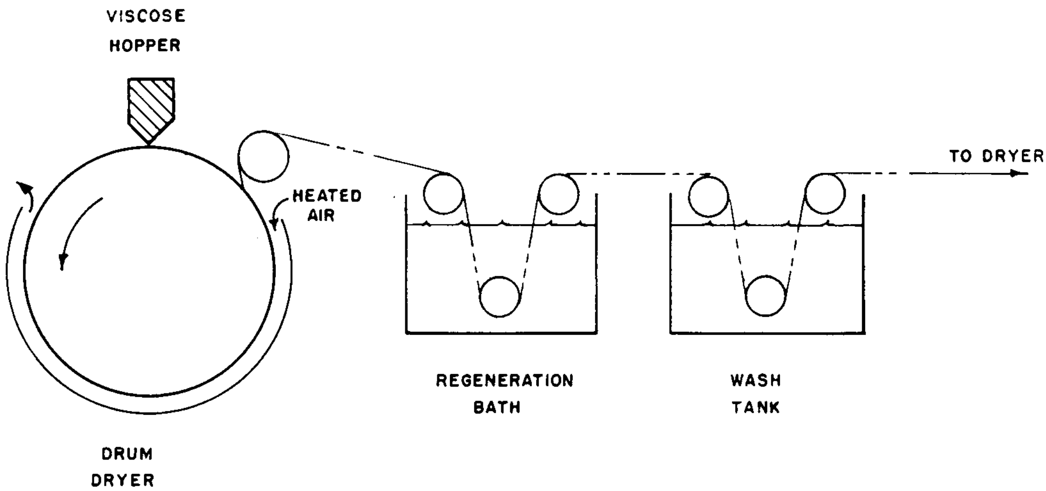

Fig. 1. Viscose dry casting process.

accomplished by a nonaqueous acid system or by heat regeneration. A hot gas or a hot nonaqueous liquid may be used for heat regeneration. If a hot gas is used, caution should be exercised in eliminating oxygen, because at elevated temperatures alkaline oxidation caused rapid cleavage of the cellulose chains and a corresponding reduction in the $\overline{DP}$ and physical properties of the film.

During regeneration of the partially dried viscose sheet, the sulfur present in the structure as xanthate is converted to water-soluble compounds. Among the compounds formed are sodium thiocarbonates and sodium sulfide. The choice of a regeneration medium depends on technical feasibility and on

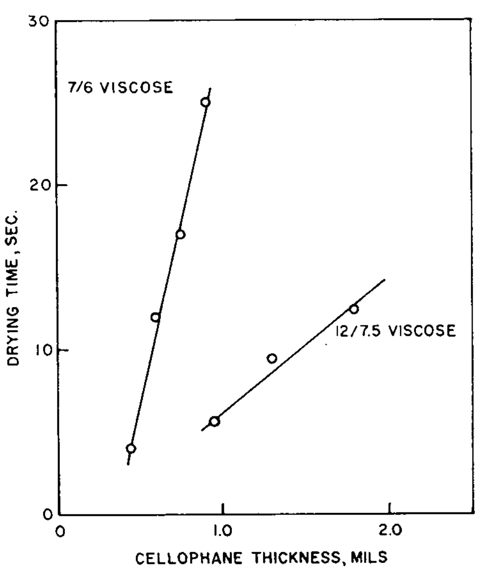

Fig. 2. Effect of film thickness on drying times for viscose films.

process economics. While regeneration with a hot gas (air) appears to be very economical, other factors do come into action such as the relative humidity of the hot gas medium. Caution should be exercised in maintaining the relative humidity of the hot gas medium at a level which does not change appreciably the condition of the sheet for the reason of processing difficulties. With liquid regeneration, factors such as bath carry-over, concentrations, etc., must be taken into consideration.

If only the chemical changes are considered, heat regeneration is simply accelerated ripening. The xanthate groups react with the free caustic in the viscose to form by-product salts. Tests with CS_2 vapor analyzers show no CS_2 vapor present over the heated viscose film. Analyses of xanthate and by-product sulfur in the film during heat drying and regeneration show conversion of xanthate to by-product sulfur without appreciable loss of total sulfur.

The temperature of regeneration is an important factor in the regeneration by heat, e.g., regeneration in a nonswelling medium. The temperature of regeneration should be high enough as to be practical, but care should be taken not to allow the temperature to become too high. Higher temperatures are less desirable because of their greater degrading action on the cellulose, particularly if any free oxygen is available. Lower temperatures may be used, but considerably longer times are required to obtain the necessary decomposition of the cellulose xanthate.

The third major step in this process entails washing and drying of the regenerated cellulose film. A simple water bath serves well to remove the salts of regeneration from the film. The compounds which were previously mentioned, formed during regeneration are very soluble in water, and may be removed with very little difficulty. As would be expected, the solubility of the regeneration products in the film increases with increasing bath temperature. The optimum bath temperature was found to be 60–80°C. The purity of the water bath should be maintained as high as is practical.

Regenerated cellulose films prepared by the conventional wet-cast method require the addition of softening agents to alleviate low durability at conditions of low temperature and low humidity. These facts introduce another advantage for film prepared by the dry-cast process, i.e., dry-cast, regenerated cellulose film exhibits high durability at conditions of low temperature and low humidity even without the addition of softening agents. The unique molecular structure of dry-cast cellulose film, which is discussed in more detail later in this paper, is responsible for the outstanding performance at these conditions. Since softener addition to the film may represent a considerable expense, dry-cast film shows a distinct advantage in this area. Softening agents may be used, if desired, with dry-cast film with some improvements in physical properties.

The drying behavior of dry-cast films also shows advantages over that for conventional film. The gel swelling, the ratio of the wet weight with surface water removed to dry weight, is approximately 2 for dry-cast film, as compared to an approximate value of 4 for conventional film. These figures indicate that the amount of moisture present in gel dry-cast film is roughly one-third of that present in wet-cast cellulose film on a dry film basis. Of course, this means that the drying load is considerably less for dry-cast film, an economic advantage.

Effect of Viscose Composition

The drying of viscose is done preferably under conditions which minimize the decomposition of xanthated cellulose. In this way the bulky xanthate groups inhibit the development of an ordered structure as water is removed. Then if regeneration is carried out in a nonswelling system, the cellulose chains are "frozen" into a disordered configuration which is desired for the maximum toughness and extensibility of the film.

During the drying period, concentration gradients are set up which result in the diffusion of electrolyte towards the heated surface of the film support. These salts crystallize at or near this surface, causing an undesirable etching of the film which reduces its transparency. This problem can be minimized by the use of low electrolyte concentration in the viscose, high solids content, and by rapid drying. Some reduction in haze is possible if the final drying of the gel film is done with the etched film surface in contact with a very smooth drying surface.

The physical properties of regenerated cellulose film prepared by the dry cast process probably best demonstrate its superiority over conventional film. The data presented in Table I show a comparison of some of the physical properties of film prepared by the two processes, wet-cast and dry-cast. The tear, the pendulum impact, and the stress flex tests have been chosen to represent the physical properties of the films. From the data it has been found that a nine- to twelvefold increase in physical properties is represented by the samples of unsoftened dry-cast film when compared to unsoftened cellophane. The comparison is based on samples of film 1 mil thick. A four- to sixfold improvement is obtained with unsoftened dry-cast film over conventional film containing softener.

The effect of variations in viscose composition on the tear strength of dry cast film yields an interesting study. The parameters to be discussed are cellulose content, degree of polymerization, CS_2 content, and caustic content. The relationship between the cellulose content of the viscose used to prepare dry cast film and the tear strength of that film is shown in Figure 3. It may be seen that the tear values increase rapidly with cellulose content from a value of 10 g. at 9%

TABLE I
Comparison of Physical Properties of Conventional and Dry-Cast Cellophane

Type Film[a]	Softener content, %[b]	Tear, g.	Pendulum Impact, kg.-cm.	Stress-flex, cycles
Conventional[a]	0	2.5	2	2
Dry-cast	0	25	18+	25
Conventional[c]	16	6	3	5
Dry-cast	14	30	18+	30

[a] All samples were 1 mil thick.
[b] Glycerol was used as softener.
[c] Laboratory cast.

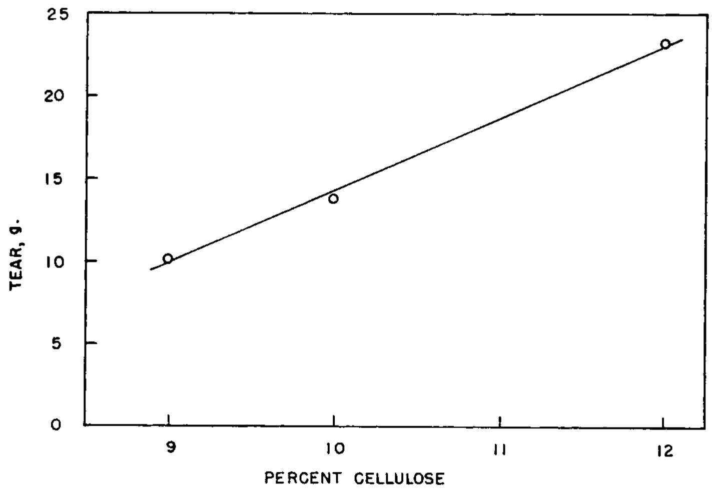

Fig. 3. Relationship between viscose cellulose content and tear strength of dry cast cellophane. Cellulose/NaOH: 1.67; 30% CS_2; $\overline{DP}$: 225; film thickness: 1 ml.

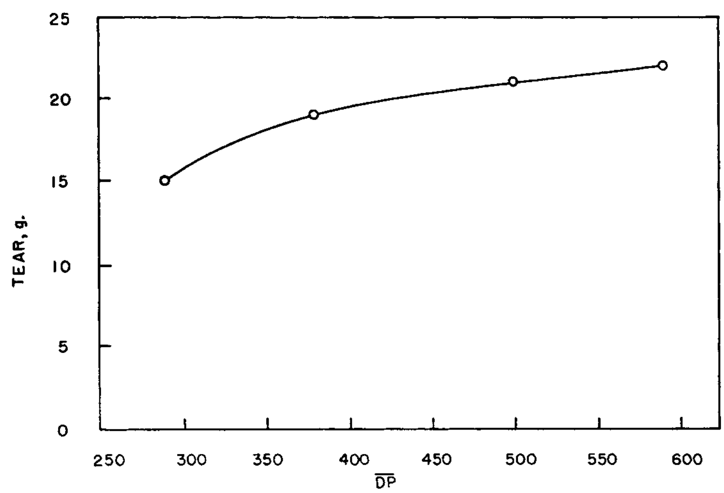

Fig. 4. Relationship between $\overline{DP}$ and tear strength of dry cast cellophane. Viscose composition: 9% cellulose, 7% NaOH; 45% CS_2; film thickness: 1 mil.

cellulose to 23 g. at 12%. This increase in durability may be attributed to the decreased mobility of the individual molecules in the more viscous viscose containing 12% cellulose leading to a less ordered structure. The viscosity of the viscose would increase roughly seven times with the 3% increase in cellulose content described above.

The relationship between the degree of polymerization of cellulose in the viscose used to prepare dry cast film and the tear strength of the resulting film is shown in Figure 4. To review only the extreme values in this figure, the tear strength increases from 15 g. at a $\overline{DP}$ of 290 to 22 g. at $\overline{DP}$ of 590 units. Again, this increase in tear strength may be attributed to increased randomization and entanglement of the individual molecules. Increasing the $\overline{DP}$ also increases the viscosity of the viscose, however. By increasing the $\overline{DP}$ from 290 to 590, the viscosity showed a twentyfold increase.

The concentration of CS_2 in the viscose used to prepare dry cast film also has a marked effect on the physical properties of the resulting film. In Figure 5 it may be seen that the tear strength increases from 11.6 to 19.0 g. with an increase in CS_2 content in the viscose from 30 to 50% based on the cellulose in the viscose. This increase is probably caused by an increase in the degree of dispersion or solution for the more highly substituted molecules.

The concentration of caustic in the viscose has a

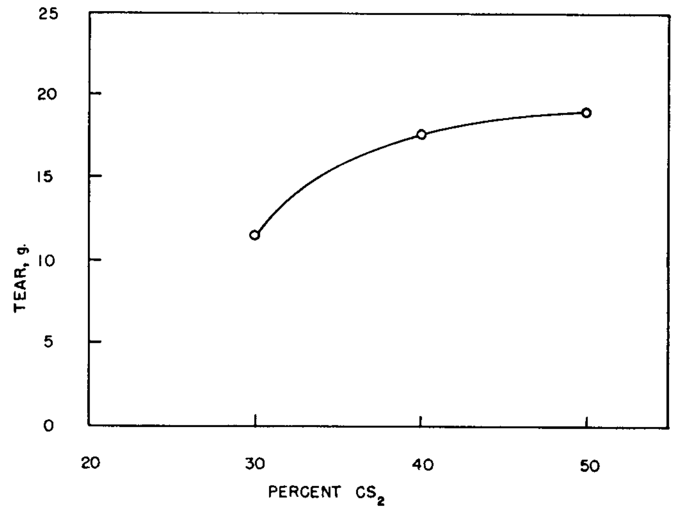

Fig. 5. Relationship between CS_2 concentration in viscose and tear strength of dry cast cellophane. Viscose composition: 10% cellulose, 6% NaOH; $\overline{DP}$: 225; film thickness: 1 mil.

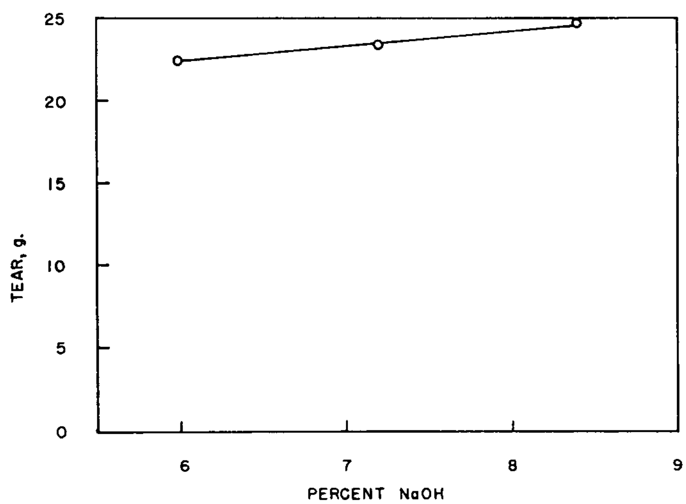

Fig. 6. Relationship between viscose caustic content and tear strength of dry cast cellophane. Viscose composition: 12% cellulose, 30% CS_2; $\overline{DP}$: 225; film thickness: 1 mil.

less pronounced effect on the physical properties of the resulting film, as shown in Figure 6. An increase in the caustic content of the viscose from 6.0 to 8.4% yields an increase in the tear strength from 22.4 to 24.7 g. However, it should be mentioned that the film clarity is generally poorer at high concentrations of caustic.

Structural Features

Like the cellulose film formed by deacetylation of cellulose acetate in a nonswelling system,[3] film dry-cast from viscose is characterized by exceptionally low lateral order. This fact has been shown by x-ray diffraction, acid hydrolysis rates, and by measurements of the degree of swelling in caustic. The process origin of the low order has already been explained. The low order is undoubtedly the most important structural variable contributing to the outstanding durability of dry cast film. Orientation in dry-cast film, like the dynamically-cast conventional cellophane, is uniplanar. Also, both exhibit a degree of uniaxial orientation, the chains aligning preferentially in the machine direction.

References

1. Nichols, J. B., U. S. Pat. 2,445,333 (Nov. 23, 1944).
2. Nichols, J. B., U. S. Pat. 2,451,768 (March 13, 1945).
3. Haskell, V. C., and D. K. Owens, *Textile Research J.*, **30**, 993 (1960).

Synopsis

Regenerated cellulose film prepared by a dry-cast method has demonstrated outstanding superiority over similar film produced by the conventional wet-cast process. Factors contributing to the superior quality of film prepared by the dry cast process are: (*1*) physical properties several times greater than for wet-cast film of corresponding thickness; (*2*) high durability at conditions of low temperature and low humidity even without the addition of softening agents, and (*3*) outstanding dimensional stability when exposed to conditions of varying temperature and humidity. The dry-cast cellophane differs structurally from the commercial product in having a lower degree of order, a lower degree of swelling in the gel form, and minor differences in molecular orientation. A commercial process for producing dry cast cellophane may be envisioned as a heated, polished support for drying the viscose film; a regenerating system of alcoholic hydrochloric acid, hot glycerine, or a hot, oxygen-free gas; a water both for purifying the film; and a conventional cellophane dryer. The ideal viscose composition for producing dry-cast cellophane is high cellulose content, moderately high $\overline{\mathrm{DP}}$, sufficient degree of substitution on the cellulose to yield a high degree of dispersion, and low caustic content.

Résumé

Les films de cellulose régénérée préparés par la méthode de fabrication par voie sèche, se sont révélés d'une qualité supérieure aux films similaires obtenus dans le processus habituel par voie humide. Les facteurs qui contribuent à la qualité supérieure des films produits par voie sèche sont: (*1*) Pour des films d'épaisseur identique les propriétés physiques sont souvent meilleures que celles des films obtenus par le procédé humide: (*2*) à basse température et faible humidité, ils possèdent une durée de vie supérieure, même sans addition d'agents de ramollissement; (*3*) ils possèdent une stabilité extraordinaire de leurs dimensions lorsqu'il sont soumis à des variations de conditions de température et d'humidité. La structure de la cellophane obtenue par voie sèche diffère de celle du produit commercial du fait qu'elle possède un arrangement moindre, un coefficient de gonflement inférieur sous forme de gel et des différences mineures dans l'orientation moléculaire. Un procédé commercial de production de cellophane par voie sèche peut s'envisager comme suit: un support chauffant et polissant qui sèche le film de viscose, un système de régénération de l'acide chlorhydrique en solution alcoolique, de la glycérine chauffée ou un gaz chaud privé d'oxygène, un bain d'eau pour purifier le film, et un séchoir conventionnel de la cellophane. La composition idéale de la viscose pour produire la cellophane par voie sèche est: une haute teneur en cellulose, un $\overline{\mathrm{DP}}$ raisonablement élevé, un degré de substitution de la cellulose suffisant afin d'obtenir un degré de dispersion élevé, et une faible teneur en base.

Zusammenfassung

Filme aus regenerierter Cellulose, die nach einer Trockengiessmethode hergestellt wurden, zeigten eine ausserordentliche Überlegenheit gegenüber ähnlichen, nach den üblichen Nassgiessverfahren hergestellten. Die Überlegenheit der Qualität des nach dem Trockengiessverfahren hergestellten Filmes ist durch folgende Faktoren gegeben: (*1*) Physikalische Eigenschaften sind mehrfach besser als für nassgegossene Filme gleicher Dicke, (*2*) hohe Haltbarkeit bei niedriger Temperatur und niedriger Feuchtigkeit auch ohne Zusatz von Weichmachern und (*3*) ungewöhnliche Dimensionsbeständigkeit bei Einwirkung wechselnder Temperatur und Feuchtigkeit. Das trockengegossene Cellophan unterscheidet sich in seiner Struktur vom handelsüblichen Produkt; es besitzt einen geringeren Ordnungsgrad, einen niedrigeren Quellungsgrad im Gelzustand und es bestehen kleine Unterschiede in der Molekülorientierung. Ein kommerzieller Prozess zur Erzeugung trocken gegossenen Cellophans wird folgende Hilfsmittel erfordern: einen erhitzten, polierten Träger zur Trocknung des Viskosefilms; ein Regenerierungssystem aus alkoholischer Chlorwasserstoff säure, heissem Glycerin oder einem heissen sauerstofffreien Gas; ein Wasserbad zur Reinigung des Films und einen normalen Cellophantrockner. Das ideale Viskosesystem zur Erzeugung trocken gegossenen Cellophans hat hohen Cellulosegehalt, mässig hohes $\overline{\mathrm{DP}}$, einen zur Erreichung eines hohen Dispersionsgrades genügenden Substitutionsgrad der Cellulose und einen gereingen Gehalt an kaustischem Alkali.