# Kinetics of Gelatinization of Cornstarch Adhesive

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## Synopsis

In the manufacture of corrugated board, thermal gelatinization of raw starch granules in the adhesive is essential for bonding setting. Kinetic studies of gelatinization of cornstarch adhesive under conditions simulating those at the corrugator revealed that the rate of advance of the gelatinization front in the starch film was linear with square root of time. A quasi-activation energy of 35.5 kJ/mol was found. The gelatinization process, above the gel point, was controlled by the rate of diffusion of water into the starch granules.

## INTRODUCTION

Water-based adhesives are used extensively in paperboard glueing operations. In the manufacture of corrugated board, starch-based adhesives are used. Unlike cold-setting emulsion or solution adhesives, which set on paperboard by dehydration,[1-4] starch adhesives set by a sequence of gelatinization and dehydration.[5,6] There are basically two types of adhesive formulations. The more common is a suspension of uncooked starch in a solution of cooked starch called the "carrier." In the other type of formulation, the starch is precooked, but incompletely. Setting of the starch adhesive requires heat and moisture for gelatinizing the raw starch granules. It is this gelatinization that provides instantaneous initial tack, and subsequent dehydration by the board (liner and medium) provides the final bond.

Even though the phenomenon of starch gelatinization has long been recognized, studies on the kinetics of starch gelatinization are very scarce. Suzuki et al.[7] reported the study of kinetics of cooking rice in which they used a parallel plate plastometer to measure compressibility of cooked rice. Kubota et al.[8] determined the gelatinization rate of rice starch by measuring the viscosity change, in a capillary viscometer, as a function of heating time. Bakshi and Singh[9] adopted colorimetry of the amylose-iodine blue complex for determining the degree of gelatinization in situ and used intact rice kernels rather than isolated starch. Recently, Wirakartakusumah reported a similar study, employing differential scanning calorimetry on rice starch.[10]

This paper deals with the kinetics of gelatinization of cornstarch in the carrier type of adhesive under conditions that simulate the setting process at the corrugator.

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## EXPERIMENTAL

### Optical Setup

When starch is gelatinized, several processes can be observed: (1) a loss in birefringence, (2) an increase in the paste viscosity, and (3) a decrease in opacity of the suspension.[11] The latter phenomenon is commonly used to determine the gel point or gelatinization temperature.[12,13] We used it here to study the rate of advance of a gelatinization front in the starch adhesive film and, by using the Kubelka-Munk theory, analyzed the data in a way similar to that used to measure the rate of penetration of liquids into porous media.[14,15]

A schematic diagram of the optical setup is shown in Fig. 1. A film of starch adhesive $E$ is applied to a glass plate $A$ placed on the aperture of a reflectometer attachment for the Spectronic 20 spectrophotometer. A heated cylinder $B$, whose base is covered by an aluminum disk $C$, which has been copper plated and blackened, serves as both a heat source and an optical background. Its temperature is controlled and monitored by a YSI telethermometer model 47. The thickness of the starch film is controlled by ring spacer $D$ made of polyester film. The cylinder is brought into contact with the starch film, and as the temperature rises to and beyond the gel point, the starch granules swell and eventually gelatinize. This causes the opacity of the starch suspension to decrease until it becomes almost transparent. The change in reflectance is monitored continuously as a function of time.

### Preparation and Characterization of Starch Adhesive

A typical formulation of carrier-type starch adhesive was prepared according to a recipe from the *Tappi* monograph Preparation of corrugating adhesive.[16] The cooked portion of starch was prepared by adding 9.1 g cornstarch (Zymaize by IGP) to 36 mL water at 43°C. While stirring, 3.0 mL 50% sodium hydroxide solution was added dropwise. When the dispersion become viscous, it was heated to 71°C for 15 min until it became a



A: supporting glass plate
B: heated cylinder
C: aluminum disc
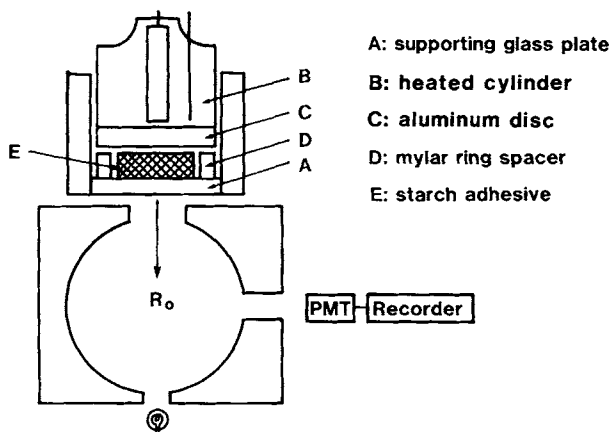D: mylar ring spacer
E: starch adhesive

Fig. 1.   Experimental setup for measuring kinetics of gelatinization of starch adhesive.

clear yellowish paste. To decrease the viscosity, 23 mL cold water was then added. The raw starch portion was prepared separately by adding 45 g cornstarch to 152 mL water at 32°C, and then 1.5 g borax ($Na_2B_4O_7 \cdot 10H_2O$) was added. The cooked portion was then poured into the raw portion while stirring. Temperature was maintained at 42°C. The solids concentration of the starch adhesive was 19.5% by weight, and its viscosity was 0.35 Pa·s at 22°C, as determined in a Brookfield viscometer. The gel point was measured by observing the disappearance of birefringence of starch granules on a hot-stage cross-polarized microscope.

### Analysis of Reflectance Data

Heat transfer from the heated cylinder to the thin adhesive film is considered to be a conduction process. During the unsteady-state heating of the film, we assumed that a front at the gelatinization temperature was moving across the film, which was considered to be made up of two layers: an opaque, ungelatinized layer, and a transparent, gelatinized layer, shown in Fig. 2. By applying the Kubelka-Munk theory,[17,18] the experimentally measured curves of reflectance versus time were converted into thickness (of gelatinized layer) versus time. See Appendix.

## RESULTS AND DISCUSSION

### Gel Point

Figure 3 shows the time required for most of the cornstarch adhesive granules to lose their birefringence at various temperatures. The gel point lies at around 68°C, which is a typical value for cornstarch adhesive.[16]

### Rate of Advance of the Gelatinization Front

Figure 4 shows reflectance-time curves of different film thicknesses at a cylinder temperature of 80°C. After the short delay required for the temperature in a layer adjacent to the cylinder to reach 68°C, the reflectance
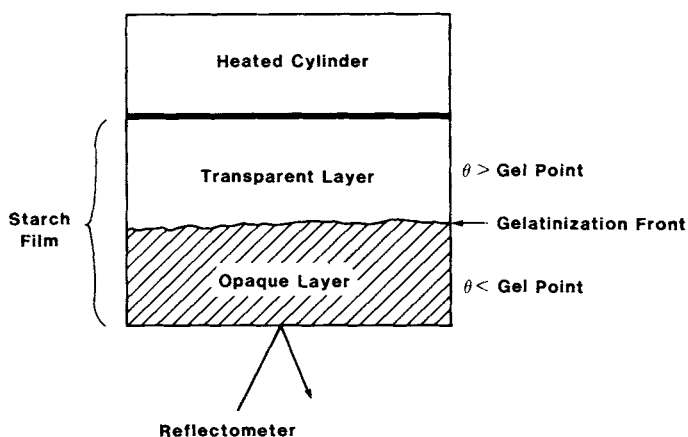
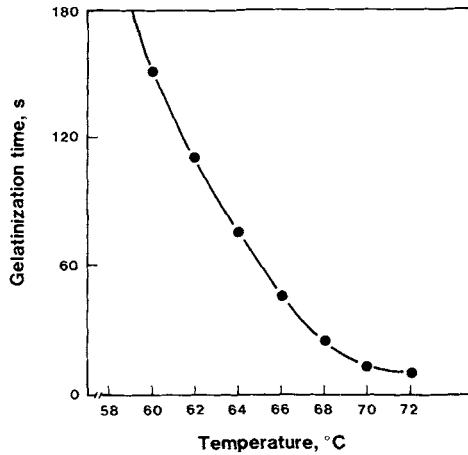Fig. 2.   Starch film during thermal gelatinization.

Fig. 3. Time required for the starch granules to lose their birefringence at various temperatures.

dropped continuously to a lower constant value corresponding to the fully gelatinized adhesive. In Fig. 5, the results have been converted into thickness of gelatinized layer versus square root time. Note the superimposition of the curves, which confirms that our assumption of an advancing gelatinization front is correct. The slope of the linear portion is then a measure of the rate of gelatinization of starch under conditions simulating the corrugating operation.

## Effect of Cylinder Temperature on Gelatinization Rate

Figure 6 shows the rate of advance of the gelatinization front of 400 $\mu$m of adhesive heated to 70, 80, 90, and 100°C. But what would be the rate of heat transfer if there were no raw starch granules in the adhesive to cause gelatinization? In other words, what would be the rate of advance of a plane
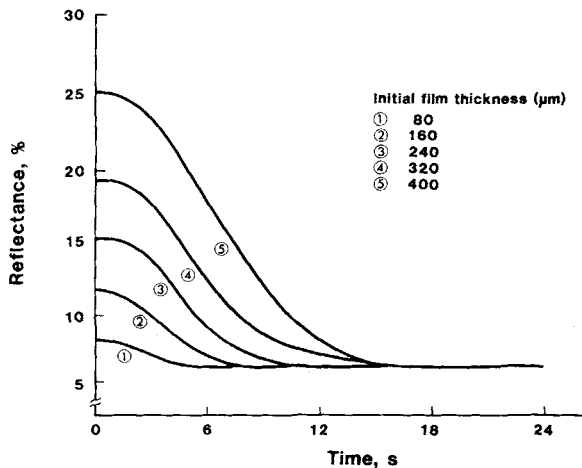


Fig. 4. Change in reflectance of starch adhesive film upon heating as a function of time for various initial film thicknesses.
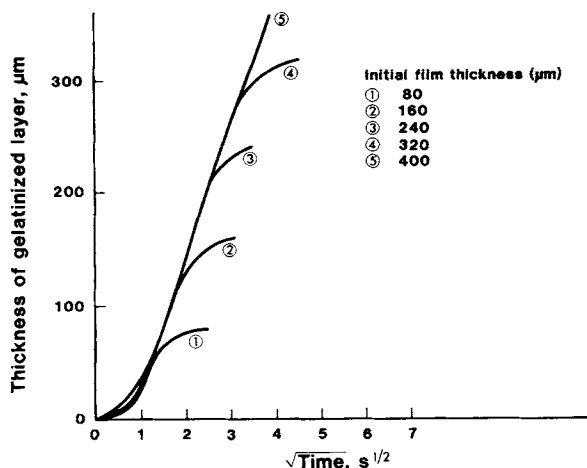
Fig. 5.   Rate of advance of the gelatinization front of cornstarch adhesive at 80°C for various initial film thicknesses.

of 68°C across a 400-μm film of cooked starch? To answer this question, a heat transfer model of the system was considered by assuming a linear flow of heat by conduction through a solid bounded by two parallel planes. For such a model, the heat transfer equation is expressed in eq. (1).[19]

$$\frac{v}{V} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n + 1} e^{-(2n + 1)^2 \pi^2 T/4} \cos \frac{(2n + 1)\pi}{2} L \qquad (1)$$
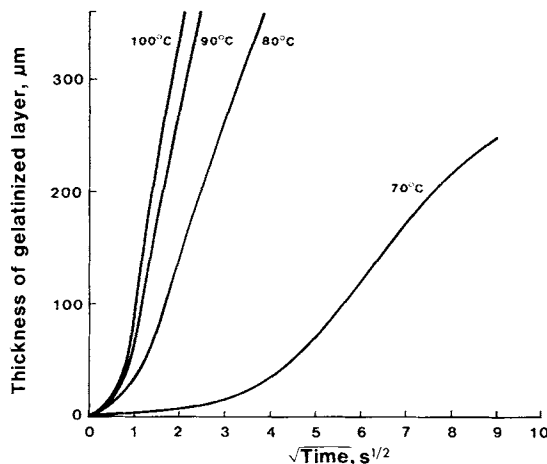
where

$$T = \frac{kt}{l^2}$$



Fig. 6.   Rate of advance of the gelatinization front of cornstarch adhesive at various temperatures.

and

$$L = \frac{d}{l}$$

where    $v$ = difference in temperature between initial and gel point
         $V$ = difference in temperature between initial and cylinder sur-
              face
         $T$ = dimensionless time
         $L$ = dimensionless distance
         $k$ = thermal diffusivity
         $t$ = time
         $l$ = thickness of the film
         $d$ = distance from the heat source

Figure 7 shows the numerical solution of eq. (1) with respect to temperature, as a function of distance from the heat source in the region $0 < L < 1$, at various dimensionless times.[19] For example, at an initial temperature of 25°C and a cylinder temperature of 80°C, $v/V = (68 - 25)/(80 - 25) = 0.66$. From the graph, after a dimensionless time of $T = 0.1$, the dimensionless distance traveled by the front is $L = 0.8$. This value of $L$ can be read off the graph at the intersection between the line for $T = 0.1$ and the horizontal line $v/V = 0.66$. When the starch film is heated at $L = 1$ by contacting it with the cylinder at temperatures of 70, 80, 90, or 100°C, the plane of 68°C advances from the point $L = 1$ to the point $L = 0$ along the horizontal line at $v/V = 0.96$, 0.78, 0.66, and 0.57, respectively. In this manner, one may construct curves showing the rate of advance of a plane at 68°C across a 400-μm film heated to various wall temperatures (100, 90, 80, and 70°C). This was done as shown in Fig. 8. Figure 9 shows the comparison between the calculated rate of advance of the 68°C front (assuming the thermal diffusivity of starch solution to be 0.00144 cm²/s) and the experimental
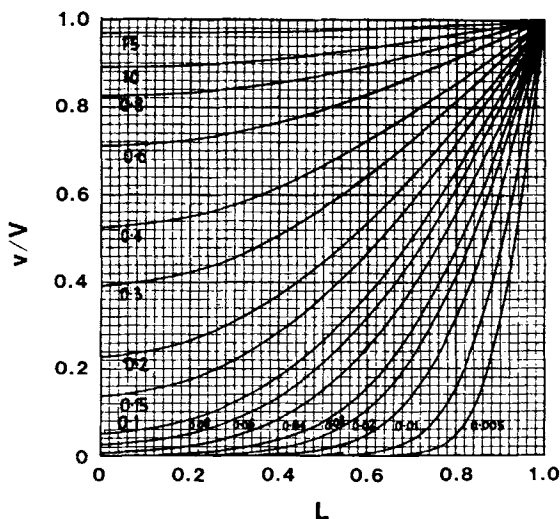


Fig. 7.   Temperature distribution at various times in the slab at $0 < d < 1$. Numbers on the curves are dimensionless times $T (= kt/l^2)$.
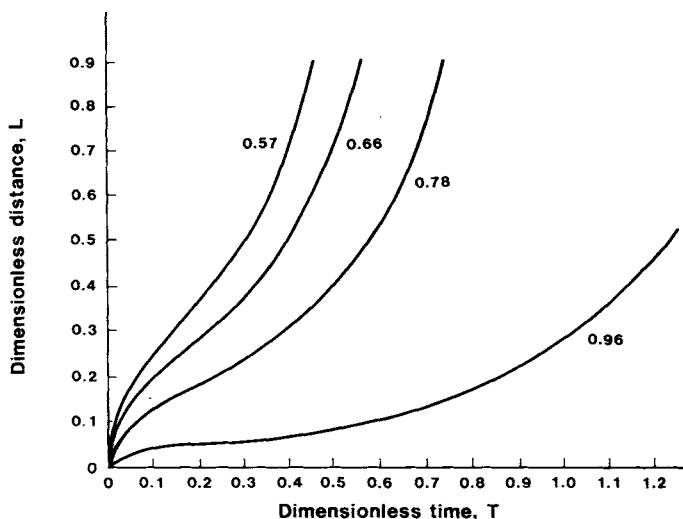
Fig. 8.   Rate of advance of a plane at 68°C across a film when the film is heated to 100, 90, 80, and 70°C, respectively. Numbers refer to values of dimensionless temperatures 100, 90, 80, and 70°C.

results. It was seen that the plane of 68°C temperature had advanced across a 400-μm film within 0.5, 0.6, 0.8, and 1.5 s at 100, 90, 80, and 70°C, respectively. When the adhesive film contains raw starch granules, however, the heat transfer is considerably delayed (experimental curves, Fig. 9) because of the gelatinization reaction. The difference in heat transfer time between the experimental and the theoretical curves may be regarded as the reaction time of gelatinization under each set of heating conditions.

## Quasi-activation Energy of the Gelatinization of Cornstarch

The gelatinization reaction of rice starch has been reported to be a first-order reaction with respect to the concentration of ungelatinized starch and
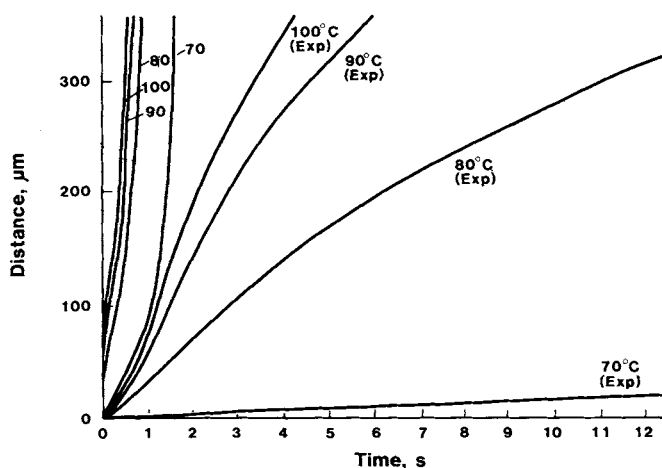


Fig. 9.   Comparison between the calculated rate of advance of the 68°C front and the experimental data.

it has been expressed as eqs. (2) and (3),[7-9] where $\alpha$ is the fraction of gelatinized starch and $K$ is the rate constant:

$$\frac{d\alpha}{dt} = K(1 - \alpha) \tag{2}$$

or

$$-\ln(1 - \alpha) = Kt \tag{3}$$

It is reasonable to assume that the gelatinization of cornstarch is also a first-order reaction. To determine whether our results satisfy eq. (3) even though they were obtained under nonisothermal conditions, we plotted $-\ln$ $(1 - \alpha)$ versus reaction time at various cylinder temperatures, as shown in Fig. 10. The fraction of raw starch, $1 - \alpha$, was obtained by taking the ratio of the thickness of the ungelatinized layer to the total film thickness. All curves, except that for 70°C, are straight lines, and therefore the slope of each line may be considered as the rate constant of the gelatinization reaction of cornstarch at 80, 90, and 100°C. The reason the curve for 70°C was not a straight line may be that the cylinder temperature was too close to the gel point, which always has some distribution, as seen in Fig. 3. Figure 11 shows a plot, similar to the Arrhenius plot, of $\log K$ versus the reciprocal of cylinder temperature. We obtained a straight-line relationship. From the slope of the curve we calculated the quasi-activation energy to be 35.5 kJ/mol, which as shown in Table I is about the same as the value reported for the gelatinization of rice starch above its gelatinization temperature.[7-9] Two values for the activation energy of the gelatinization of rice starch,
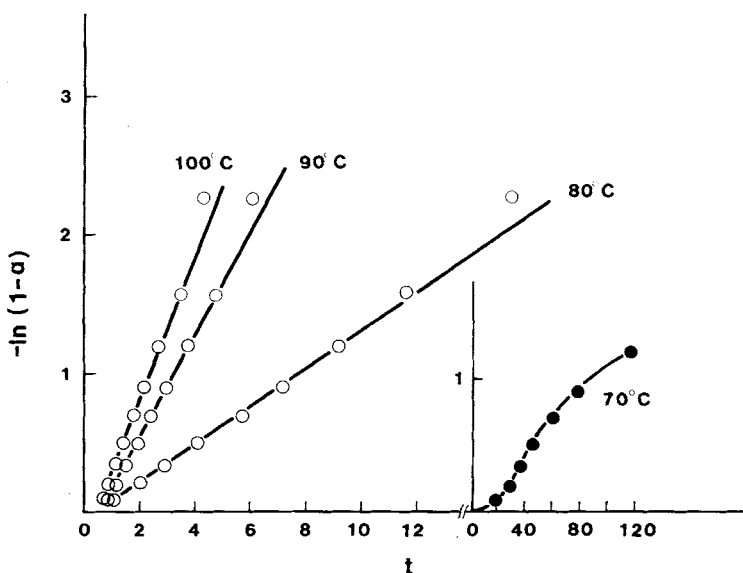


Fig. 10. Relationship between $-\ln(1 - \alpha)$ and reaction time for various cylinder temperatures.
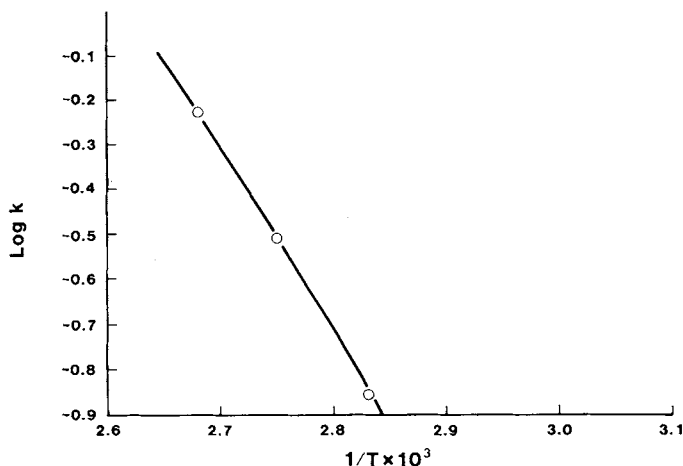
Fig. 11.  Relatinship between log $k$ and the reciprocal of cylinder temperature.

depending on the temperature range, have been reported. It is considered that below the critical temperature the gelatinization process is controlled by the chemical reaction of starch with water, and above the critical temperature it is controlled by the diffusion of water into the starch granules.[7-9] Therefore we conclude here that the gelatinization process of cornstarch adhesive above the gel point is controlled by the rate of diffusion of water into the starch granules.

## CONCLUSIONS

The rate of advance of gelatinization front of starch adhesive can be determined by measuring the reflectance of gelatinizing film and by converting it into the film thickness of the gelatinized layer using the Kubelka-Munk theory for a two-layer system. It was found that the rate of advance of the gelatinization front was linear with square root of time.

The kinetics of gelatinization of cornstarch adhesive were studied under unsteady-state conditions by using a heat transfer model, and a quasi-activation energy of gelatinization of 35.5 kJ/mol was obtained. It is very close to the value reported in the literature for rice starch.

It is concluded that the gelatinization process above the gel point is controlled by the rate of diffusion of water into the starch granules.

TABLE I

Activation Energy Data for Various Starches in Two Temperature Ranges[a]

| Rice | Activation energy (kJ/mol) | |
|---|---|---|
| | 50–85°C | 85–120°C |
| Rough | 77.5 | 44.0 |
| Brown | 103.5 | 40.2 |
| | 75–100°C | 100–120°C |
| Japanese | 79.6 | 36.9 |

[a] From Refs. 7–9.

## APPENDIX

The basic equations of the Kubelka-Munk theory[18] for multilayer systems are expressed by

$$R_x^{\Sigma i} = \frac{[R_x^{\Sigma(i-1)} - R_\infty^i] + R_\infty^i[1 - R_\infty^i R_x^{\Sigma(i-1)}] \exp\,(1/R_\infty^i - R_\infty^i)\,S^i d^i}{[R_x^{\Sigma(i-1)} - R_\infty^i]\,R_\infty^i + [1 - R_\infty^i R_x^{\Sigma(i-1)}] \exp\,(1/R_\infty^i - R_\infty^i)S^i d^i} \quad \text{(A.1)}$$

$$S_i = \frac{1}{d^i(1/R_\infty^i - R_\infty^i)} \ln\left[\frac{R_\infty^i - R_x^{\Sigma(i-1)}}{R_\infty^i - R_x^{\Sigma i}}\right]\left[\frac{1/R_\infty^i - R_x^{\Sigma i}}{1/R_\infty^i - R_x^{\infty(i-1)}}\right] \quad \text{(A.2)}$$

$$R_\infty^i = \frac{b - \sqrt{b^2 - a^2}}{2a} \quad \text{(A.3)}$$

where $\quad a = R_{x1}^{\Sigma i}\,R_{x2}^{\Sigma(i-1)} - R_{x1}^{\Sigma(i-1)}R_{x2}^{\Sigma i}$

$$R_\Sigma^i = 1 - \frac{k^i}{S^i} - \left[\frac{2k^i}{S^i} + \left(\frac{k^i}{S^i}\right)^2\right]^{1/2} \quad \text{(A.4)}$$

where $\quad R_x^\Sigma i \quad$ = reflectance of combined $i$ layers over the background of reflectance $x$

$R_x^{\Sigma(i-1)} \quad$ = reflectance of combined $(i - 1)$ layers over the background $x$

$R_\infty^i \qquad$ = reflectivity of $i$th layer

$S^i \qquad$ = light-scattering coefficient of $i$th layer

$d^i \qquad$ = thickness of $i$th layer

$K^i \qquad$ = absorption coefficient of $i$th layer

To determine the reflectance of two layers (gelatinized and ungelatinized) combined over the black background, we first calculated, from eq. (A.3), the reflectivity $R_\infty^1$ and $R_\infty^2$ of each gelatinized and ungelatinized layer by measuring reflectance of each layer over a black background and over a white background. In this application,

$R_{x2}^{\Sigma i} \qquad$ = reflectance of gelatinized layer over a black background

$R_{x1}^{\Sigma i} \qquad$ = reflectance of gelatinized layer over a white background

$R_{x2}^{\Sigma(i-1)} \quad$ = reflectance of ungelatinized layer over a black background

$R_{x1}^{\Sigma(i-1)} \quad$ = reflectance of ungelatinized layer over a white background

We then calculated from eqs. (A.2) and (A.4), light-scattering coefficients $S^1$ and $S^2$ and the light absorption coefficients $K^1$ and $K^2$ of the gelatinized and ungelatinized layer, respectively.

Once all the parameters $R_\infty^1$, $R_\infty^2$, $S^1$, $S^2$, $K^1$, $K^2$, and $R_{x1}$, $R_{x2}$ had been found, we calculated overall reflectances of various combinations of two layers and constructed sets of curves for converting reflectances into thicknesses, as shown in Fig. 12. Figure 4 was then transformed into Fig. 5,
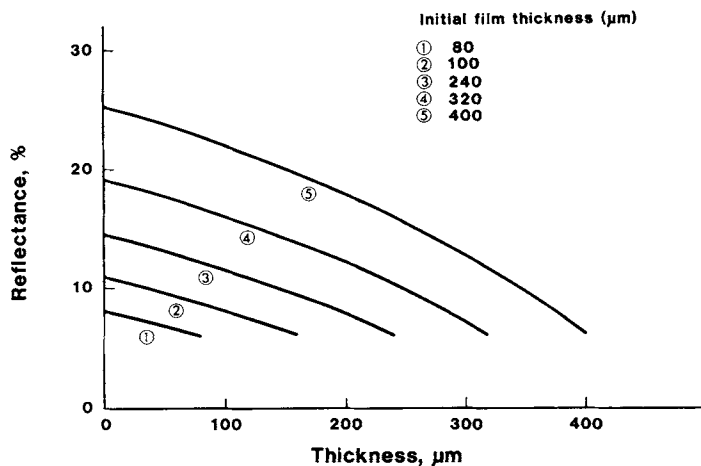
Fig. 12. Relationship between reflectance of a starch film made of two layers (gelatinized and ungelatinized) and thickness of gelatinized layer for various initial film thicknesses.

which shows the rate of advance of the gelatinization front of cornstarch adhesive at various initial thicknesses upon heating at 80°C.

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