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ABSOLUTE MEASUREMENTS OF THE RHEOLOGICAL PROPERTIES OF STARCH DURING GELATINIZATION

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The method af the absolute measurement of the rheological properties of the starch suspension during gelatinization is presented. It takes the advantage of the results of simple one-point measurement of absolute pasting characteristics and gives a possibility of calculating the multi-point flow curves.

INTRODUCTION

The properties of gel which are the final stage of the hydrothermal modification of starch are well known [1-7]. However, it is not too much known on the course of gelatinization from the point of view of changes of rheological properties. This situation results from the lack of a suitable, correct measurement method. Aqueous suspension of nongelatinized starch grains is a typical dispersion with a strong tendency towards sedimentation. On the gelatinization at an increasing temperature an intensive stirring is necessary at least in the preliminary step of the procedure in order to maintain a homogenicity of suspension. Under such nonisothermal, and first of all turbulent flow, absolute viscosimetric methods are unsuitable [8]. As a matter of fact the standard empirical, method has been used for years for the measurement of the characteristics of pasting. It provides a comparison of various behaviours of starch under given experimental conditions [9, 10]. From the rheological point of view such results are unlikely as they have a little physical sense. More reliable results are available from the Winkler's method of the measurements of absolute pasting characteristics [11, 12]. It is an exemple of absolute one-point run in which apparent viscosity of starch paste is obtained under constant rate of shear (or shear stress) at any temperature. The Winkler's method is formally correct, however any univocal interpretation of changes observed on gelatinization is impossible. The properties of non-Newtonian liquids may only be described using the absolute as well as the multi-point method.

This situation prompted me towards invention of a measurement method providing the rheological identification and the description of processes which take place on gelatinization of starch. The method takes the advantage of the results of simple one-point measurement of absolute pasting characteristics and gives a possibility of calculating the multi-point flow curves.

MATERIALS AND METHODS

The measurements were carried out using rotary, high sensitive, co-axial viscometer working with constant torque [13]. The simple method of the measurememt of absolute pasting characteristics was described in details in an early presented paper. The 1.5% aqueous suspension of potato starch was investigated.

RESUTLTS

The characteristics of pasting were run for 6 different torques. The results are presented in Fig. 1 as the reciprocal of angular velocity of the rotor. Ω^{-1}, versus the temperature, T, and time, t. The velocities, Ω_i, related to corresponding torques, M_i, were found for each temperature using the above diagrams. The procedure is illustrated therein. Coordinates, M_i, Ω_i, for 6 points were found on this manner for any arbitrary temperature in the range between 78 and 94°C. Hence flow curves which characterize rheological properties of the formed paste could be derived. The shear stress, τ. and Newtonian (uncorrected) rate of shear $\dot{\gamma}_n$, were calculated using known relations. Flow curves obtainable in this manner are presented in Fig. 2. The changes of the pattern of these flow curves illustrate a variation of rheological properties which take place on gelatinization of starch suspension. The curve for the lowest available temperature i.e. for 78°C is almost a straight line with its intercept in the origin of coordinates. It means that at this stage of gelatinization suspension saves its Newtonian character. As the temperature increases flow curves become more nonlinear. Its characterirstic shape points to the gradual increase of the contribution from the non-Newtonian effect of shear-thinning. The properties of gelatinized suspension undergo subsequent qualitative change over 84°C. The curves start beyond origin of the coordinate system: they start at gradually icreasing values of shear stress. The effect of the formation of the yield stress, τ_y, characteristic of viscoplastic systems delivers the argument that a rigid structure resistant to shear is formed inside the paste.

The quantitative approach to the obtained flow curves was done using the power law [14], commonly used in the rheology of starch. Three parameter modification of the power law which involves viscoplastic effect of the yield stress has been proposed by Charm [15]:

$$\tau = \tau_y + K\,(\dot{\gamma})^n \tag{1}$$

where: τ_y, K and n are experimental constants.

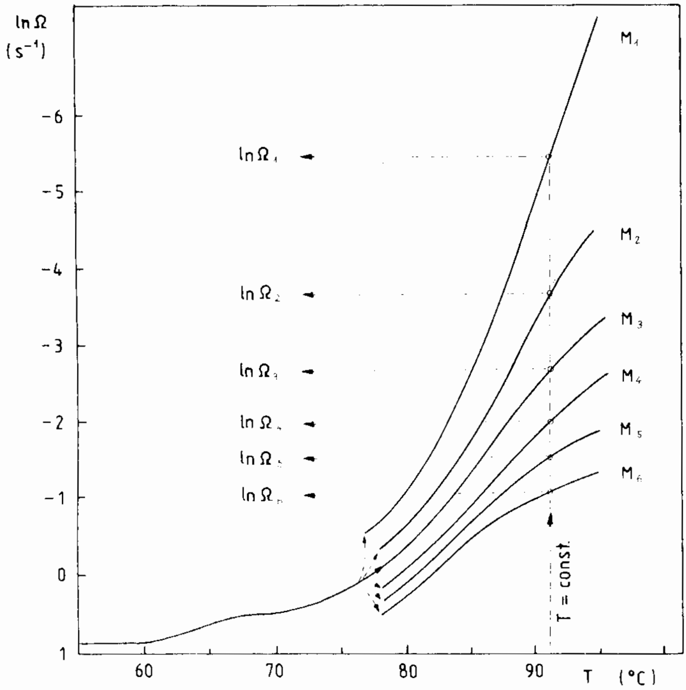

Fig. 1. The mode of the determination of coordinates of the points of flow curves for certain temperature, T

The fitting was fund that this approach is fully suitable for the describing of the flow curves within the entire available range of temperatures. Hence the gelatinization may be presented in the form of temperature changes of the parameters of this model. Determined functions n(T), K(T) and $\tau_y(T)$ are presented in Fig. 3 a-c.

The power law coefficient n reflects the dissimilarity of the liquid under study to Newtonian liquid. It decreases monotonically as the function of the temperature in the entire investigated range. The n value decreases from 0.95 at 78°C (the liquid is almost Newtonian) to 0.53 at 93°C. The K constant, called the consistence constant, increases monotonically in that range. Viscoplastic properties of paste which are expressed by the formation of the yield stress, τ_y, appear rather suddenly at 83°C. The stress increases very fast and reaches 0.6 Pa at 93°C.

Variations of K and n parameters with the temperature strongly correalate with one another: lnK is the linear function of n. Hence the power law can be presented in a modified form:

$$\tau = \tau_y + \tau_O (\dot{\gamma}/\dot{\gamma})^n \qquad (2)$$

were: τ_O and $\dot{\gamma}_O$ are experimental constans.

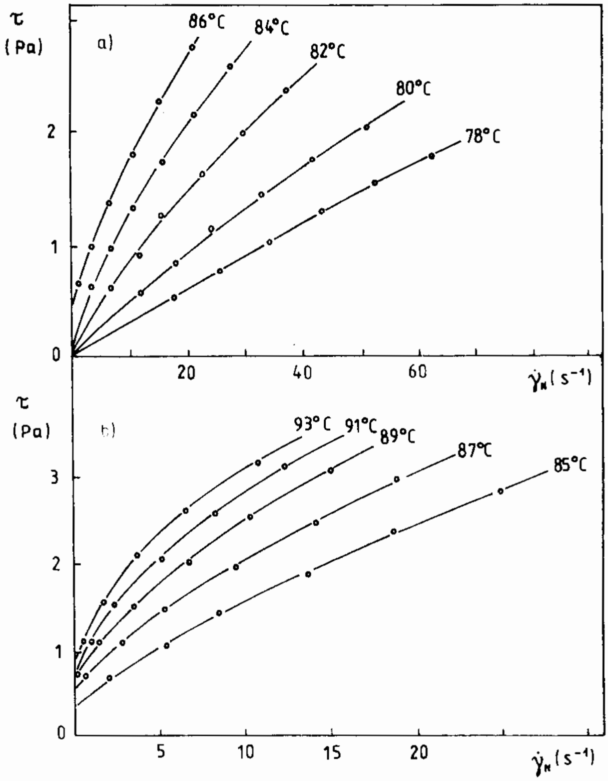

Fig. 2. The change of the pattern of flow curves of starch suspension during the gelatinization in the range; a) 78-86°C, b) 85-93°C

This equation describes the rheological properties of starch suspension in each stage of the gelatinization. It takes a new meaning. It does not contain the consistence constant, K, anymore. It is replaced by τ_O in the units of shear stress and γ_O in the units of the rate of shear. These parameters characterize rheological properties of the starch suspension of a given concentration independently of a degree of gelation. As the temperature increases only both power n and yield stress, τ_y, change.

DISCUSSION

The described method is the only method providing observation and description of changes of rheological properties of pasting starch suspension. This method exploiting the technique of the measurement of absolute pasting characteristics allows to determine the shape of a flow curve at any temperature. Because of specific conditions of the hydrothermal gelatinization of starch such results cannot be obtained by direct measurements if the typical experimental methods are involved. The simplicity of the measurements is achieved by using the rotor of the described construction. The preliminary phase of the gelatinization

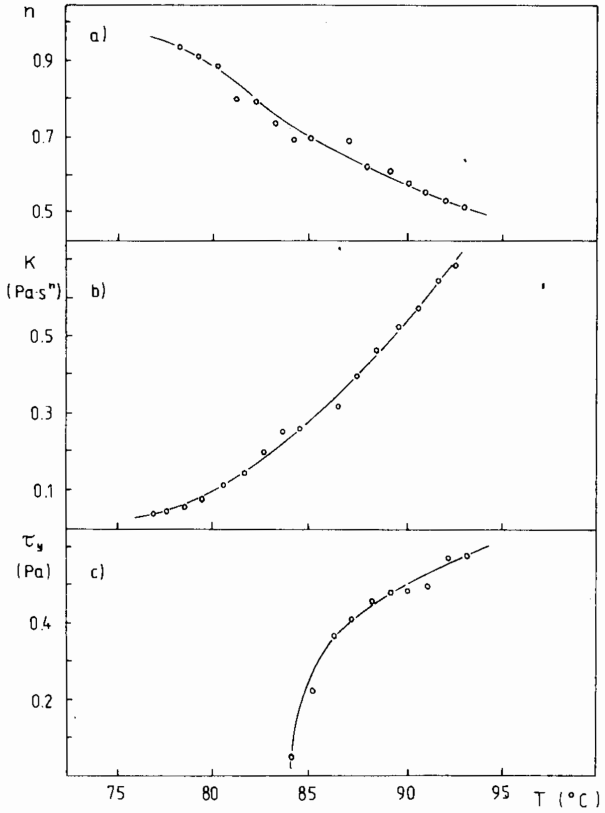

Fig. 3. Temperature functions of parameters of the power law; a) n — power law coefficient, b) K — consistence constant, c) τ_y — yield stress

may not be observed if the homogenicity of samples takes intensive stirring. It is, however, not too serious fault because as it is shown by the analysis of the results such suspension behaves as a simple dispersion with Newtonian properties.

The fully satisfactory description of rheological properties of the gradually developed structure of paste is provided by four — parameter mathematical model (Eq. 2) being the modified power law. Temperature functions which appear in the model of n and τ_y parameters are the coorect illustration of the evolution of properties of the pasting suspension: a turn from Newtonian liquid ($n = 1, \tau_y = 0$) through non-Newtonian liquid shear-thinning ($n < 1, \tau_y = 0$) into nonlinear viscoplastic liquid ($n < 1, \tau_y > 0$). The τ_O and $\dot{\gamma}_O$ constant of values independent on the phase of the gelatinization characterize properties of the starch suspension under study.

The power law in the presented form is not the only empirical formula anymore. It has a deeper rheological sense of the state equation [14]. Almost identical model without τ_y parameter has already been used in the rheology of starch. Schutz has adopted it for describing of the enzymatic degradation of the structure of starch gel [16].

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ABSOLUTNA METODA POMIARU WŁAŚCIWOŚCI REOLOGICZNYCH KLEIKUJĄCEJ SKROBI

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Streszczenie

Przedstawiono absolutną metodę pomiaru reologicznych właściwości kleikującej suspensji skrobiowej. Wykorzystując wyniki prostych, jednopunktowych pomiarów absolutnych charakterystyk kleikowania, wyznaczenie wielopunktowych krzywych płynięcia $\tau(\dot{\gamma})$. Przeprowadzone badania 1.5% wodnej suspensji skrobi ziemniaczanej wykazały, że dopiero dla temperatury przekraczającej o kilkanaście stopni początek kleikowania, tworzący kleik zaczyna wykazywać cechy cieczy rozrzedzanej ścinaniem o granicy płynięcia τ_y. Zadowalający opis danych doświadczalnych uzyskano wykorzystując zmodyfikowaną, 4-parametrową postać prawa potęgowego: $\tau = \tau_y + \tau_o (\dot{\gamma}/\dot{\gamma}_o)^n$. Temperaturowe zależności parametrów n i τ_y jednoznacznie określają obserwowaną ewolucję właściwości kleikującej suspensji: przejście od cieczy newtonowskiej, przez ciecz rozrzedzaną ścinaniem, aż do nieliniowej cieczy plastycznolepkiej.