On the Use of an Internal Mixer For the Rheological Characterizattion of Maize Starch

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Abstract:
The rheological behaviour of hydrated maize starch is investigated by means of a Haake internal mixer equipped with a sealed chamber. Results were obtained at temperatures between 89 and 115°C with water content between 25 and 30%. Through a proper calibration torque measurements and rotation speeds are converted to shear stress and shear rate data and this leads to the plot of a flow curve in the 10 - 1000 s^{-1} range. The data are compared with results of capillary rheometer and show that the mixer enables a reproducible plastification of the maize starch. The viscosity of the maize starch in the high shear rate range can be described by an apparent power law taking into account the moisture and temperature effects. On a larger range of shear rate, a Carreau law is preferred but the dependence on the temperature can only be described with shift factors that require a moisture dependent activation energy. Finally, this later discrepancy can be avoided by using a reference temperature to fulfil the iso-free volume condition by taking a constant temperature difference towards the glass transition of the samples. The glass transition is calculated by the Couschman and Karasz equation.

Zusammenfassung:
Das rheologische Verhalten hydrierter Maisstärke wird hier mit Hilfe eines Haake „internal mixer", ausgestattet mit einem „sealed chamber" untersucht. Ergebnisse wurden für Temperaturen zwischen 89 und 115°C, bei einem Wassergehalt von 25 und 30% erhalten. Unter Ausnutzung einer geeigneten Kalibriermethode lassen sich die Drehmoment-Messungen und Rotationsgeschwindigkeiten in Scherspannungen und Scherraten umrechnen, so dass sich Fliesskurven im Bereich von 10 - 1000 s^{-1} ergeben. Die Daten werden mit Messungen an einem Kapillarrheometer verglichen. Dabei zeigt sich, dass der Mischer eine reproduzierbare Plastifizierung der Maisstärke zulässt. Die Viskosität der Maisstärke lässt sich im Bereich hoher Scherraten durch ein Potenzgesetz-Verhalten beschreiben, welches Feuchtigkeits- und Temperatureffekte berücksichtigt. Über einen grösseren Bereich von Scherraten wird ein Carreau-Gesetz bevorzugt, aber die Temperaturabhängigkeit lässt sich dann nur über Korrekturfaktoren modellieren, die feuchtigkeitsabhängige Aktivierungsenergien enthalten. Diese Diskrepanz lässt sich auflösen, indem eine Referenztemperatur verwendet wird, bei der gleiche freie Volumina vorliegen, indem ein konstanter Temperaturabstand zur Glasübergangstemperatur der Proben als Referenz gewählt wird. Die Glasübergangstemperatur wird dabei nach der Gleichung von Couschman und Karasz erhalten.

Résumé:
Le comportement rhéologique d'amidons de maïs hydratés a été analysé à l'aide d'un mélangeur interne Haake équipé d'une chambre étanche pour des températures comprises entre 89 et 115°C et des taux d'humidité variant entre 25 et 30%. Une calibration adéquate permet de convertir les valeurs de couple et de vitesse en contrainte et gradient de vitesse de cisaillement pour obtenir finalement une courbe d'écoulement entre 10 et 1000 s^{-1} . Les données sont comparées avec des résultats de rhéométrie capillaire et montrent que le mélangeur permet d'obtenir une plastification reproductible et contrôlée de l'amidon. La viscosité à haut gradient de vitesse de l'amidon de maïs peut être décrite par une loi puissance prenant en compte les effets de la température et de l'humidité. Sur un domaine élargi de gradients de vitesse, une loi de Carreau est préférable mais la dépendance à la température requiert l'utilisation de facteurs de translation décrits par une énergie d'activation qui dépend de l'hydratation. En fait, ce problème peut être résolu par l'utilisation d'une température de référence qui satisfasse une condition d'iso-volume libre par l'utilisation d'une différence de température constante par rapport à la transition vitreuse des échantillons. Cette température est calculée par l'équation de Couschman et Karasz.

Key Words: Starch, Internal Mixer, Rheology, Capillary Rheometer

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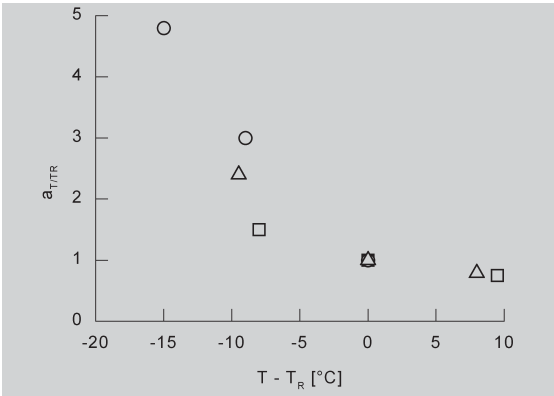
Table 3 (above): Glass temperature, theoretical and practical reference temperature.

Water content [%]	T_g [°C]	$T = T_g + 95$ [°C]	T_R [°C]
25	21	116	115
27.5	10	105	107
30	0	95	97.5

Figure 8 (below): Shift factors in an iso-free volume condition or different reference temperature (115 (O), 107 (Δ), and 97.5 °C (□)). The corresponding glass transitions are such that the temperature difference toward T_g is constant and equal to 95 °C.



zontal shift factors a_{T/T_R} from the measurements in the internal mixer yields a single curve. In order to check this assertion, the glass transition of the hydrated starch were calculated using the Couschman and Karasz equation [21] according to the work of Orford et al.[22] and Kalichevsky et al.[23]:

$$T_g = \frac{HT_{gH_2O}\Delta C_{pH_2O} - (1-H)T_{gStarch}\Delta C_{pStarch}}{H\Delta C_{pH_2O} - (1-H)\Delta C_{pStarch}} \quad (7)$$

with $\Delta C_{pH2O} = 1.94$ J/g, $\Delta C_{pStarch} = 0.47$ J/g, T_{gH2O} = 145°K, and $T_{gStarch}$ = 500°K.

Tab. 3 summarizes the glass transition of the different samples. The shift factors were evaluated at the temperature T_R, as close as possible to the temperature T such as $T - T_g$ = 95°C. Fig. 8 gives a plot of the shift factors as a function of $T - T_R$ which gives a single mastercurve in the range of uncertainty of the measurements and glass transition. This could also be written:

$$\eta(115^\circ C,\ 25\%\ H_2O) = \eta(107^\circ C,\ 27.5\%\ H_2O) = \eta(97.5^\circ C,\ 30\%\ H_2O) \quad (8)$$

4 CONCLUSION

The renewed interest on the development of biopolymers for food packaging purpose has been rapidly growing in the past years. In the earliest attempt, these materials were blended with conventional thermoplastic polymers in order to promote the fragmentation of plastics like polyethylene for short term use in agricultural applications. However, this solution has turn to be unsafe and the interest has now focused on fully biodegradable materials such as starch and its derivative.

The key problem is to obtain low cost products. Maize flour is an interesting material from this point of view since its price is competitive with that of conventional commodity polymers. Nevertheless a low final cost could only be achieved if the maize flour may be processed with classical techniques such as film blowing or cast film extrusion with only minor changes within the tools and process. For this purpose, there is a firstly need to get a better understanding of the phenomena that are involved during the plastification of such polymers in presence of plasticizers such as water or glycerol. Secondly, the knowledge of their rheological behaviour in the melt is certainly an obliged step for a proper design of the tools (screws and dies) that will be required.

The problem is quite complicate since the evaluation of the rheological behaviour of hydrated maize starch in the intermediate temperature and moisture range (90 °C < T < 120 °C and 0.25 < H < 0.35) requires the plastification of the samples. In addition, these measurements must be performed during or just after the gelatinization has occurred otherwise the resulting gel hardly flows. For these reasons, special devices such as instrumented dies following screw extrusion or a Couette mixer are described in the literature.

In this paper, this investigation is carried out in an internal mixer. After proper calibration, this enables to get a flow curve that is consistent with results from the literature. Various equations describing the variation of the viscosity with shear rate and taking into account the effects of both the temperature and the water content are described in relation to similar data from various authors. The complex dependence of the rheological behaviour on variables such as temperature, time and moisture can be greatly simplified by the use of an iso-free volume condition. In this condition, the viscosity at any reference temperature, such that the temperature difference towards the glass transition temperature is constant, should be identical. Indeed, the glass transition temperature itself contains the essential features of the influence of the water on the rheology of these materials.

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