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NON-NEWTONIAN BEHAVIOR OF AMYLOSE-AMYLOPECTIN MIXTURE SOLUTION*

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and Naomichi Iso*¹

This study aimed to clarify the viscometric properties of starch solution from the point of view of the composition ratio of amylose and amylopectin. The viscosities of dilute solutions of amylose and amylopectin were measured at 25°C. The viscosity of a concentrated solution of a mixture of amylose and amylopectin was measured at various temperatures to obtain the activation energy of flow. The intrinsic viscosity, $[\eta]$, and Huggins' constant, k' , were 0.87 dl/g and 0.54 for amylose and 1.22 dl/g and 2.46 for amylopectin, respectively. The flow properties and the activation energy of flow of the concentrated mixture solution were proportional to the ratio of amylose and amylopectin and coincided with those of the native starch solution in the same composition. Thus it was found that additivity existed between flow properties and activation energy of flow of amylose and amylopectin. Non-Newtonian behavior, dilatant flow of concentrated amylose solution and thixotropic flow of concentrated amylopectin one, were observed. Those solution properties were considered to come independently from their molecular conformation.

Key words: Starch, Amylose, Amylopectin, Viscosity, Non-Newtonian flow

Introduction

It is well known that starch granules are composed of amylose and amylopectin. The concentrated solution properties of starch are considered to alter according to the composition ratio of amylose and amylopectin. The studies on the structures and physico-chemical properties of amylose and amylopectin have been done, individually, in water (Husemann *et al.*¹⁾; Burchard²⁾); potassium hydroxide solutions (Cowie *et al.*^{3), 6)}; Everett *et al.*^{4), 5)}); and potassium chloride solutions (Cowie⁶⁾⁻⁸⁾). However, there are few studies on the concentrated solution properties of starch from the point of view of the composition ratio.

This study aimed to clarify the viscometric properties of native starch solution and model solutions made by mixing amylose and amylopectin in several ratios.

Experimental

Samples

An amylose sample was obtained from corn starch by the butanol precipitation method (Schoch⁹⁾). As a sample of amylopectin, waxy corn starch was used. Although the waxy corn starch used here contained approx. 4% amylose, the amylose content was considered to be negligible for the purpose of this work. Model solution samples were prepared by mixing the separated amylose and the amylopectin, *i.e.* waxy corn starch. In addition, two kinds of high-amylose corn starch, 72 wt% and 51 wt% of amylose content, and corn starch, 23 wt% of amylose content, were used as native samples.

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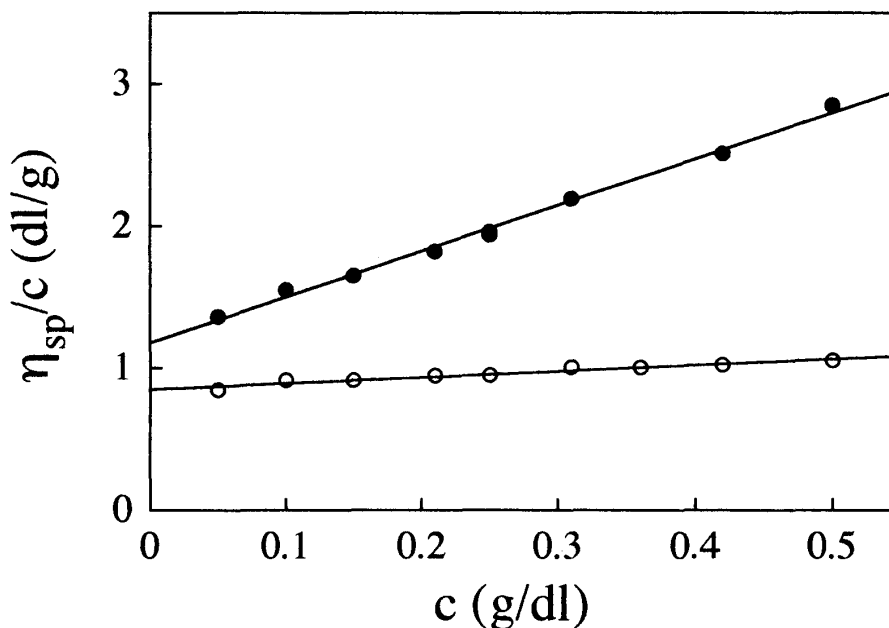


Fig. 1. The Huggins' plot of amylose (open circle) and amylopectin (closed circle) in dimethylsulfoxide (DMSO) at 25°C.

The amylose and/or amylopectin and native starch were dissolved in dimethyl sulfoxide (DMSO) by stirring for 3 days at room temperature. All the original starch samples used in this work were supplied by Nippon Starch Chem. Co., Ltd.

Viscosity measurements of dilute solutions

The viscosities of the dilute solutions were measured using an Ubbelohde type viscometer, in which the flow time of water was approx. 150 s at 25°C. The concentration range of the solutions was from 0.05 to 0.5 g/dl.

Viscosity measurements of concentrated mixture solutions

The viscosities of the concentrated mixture solutions, of which the concentration ranged from 3.0 to 5.0 g/dl, were measured using an U-rheometer (Iwamoto Co., Kyoto). This viscometer was a Couette type rotational viscometer: the radii of the outer and inner cylinders were 1.50 cm and 1.25 cm, respectively. The diameters of wire used here were 0.4 mm and 0.5 mm, of which the wire constants were 1.01×10^3 and 4.17×10^2 dyn·cm/deg, respectively. The rotational speed of the outer cylinder was 50–350 rpm, *i.e.*, shear rate of 34–240 s^{-1} , and the measurement temperatures were at 25, 40, 55, and 70°C.

Results and Discussion

The results of viscosity measurement of dilute solution were analyzed using the Huggins equation:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c + \dots \quad (1)$$

where η_{sp}/c is the reduced viscosity and c is the concentration. Figure 1 shows Huggins' plot of amylose and amylopectin solutions: the abscissa was the concentration of starch solution and the ordinate was the reduced viscosity. The Huggins' plot of the sample solutions exhibited a linear function to the concentration. Thus intrinsic viscosity, $[\eta]$, and Huggins' constant, k' , were obtained from the intercept and the slope of the straight line, respectively. As shown in Table 1, the k' of

amylopectin solution is greater than that of the amylose one. Thus each amylopectin molecule was considered to interact more strongly relative to each amylose one because the constant k' is known to relate to the degree of intermolecular interaction. The greater value of k' of amylopectin was consistent with the fact that the value of $[\eta]$ of amylopectin was greater than that of amylose, as described in Table 1.

The concentrated solutions (which are 4% concentration of amylose and amylopectin) exhibit the non-Newtonian flow as shown in Fig. 2. In general, the following power law exists between shear rate, $\dot{\epsilon}_t$, and shear stress, p_t , for the non-Newtonian flow.

$$p_t = k\dot{\epsilon}_t^n \quad (2)$$

where k and n are constants. The constant, n , is particularly known as an index of non-Newtonian flow in solutions. In the case of Newtonian flow, shear stress is directly proportional to shear rate, *i.e.*, $n=1$, in the equation of p_t . In the case of non-Newtonian flow on the other hand, n -value is not equal to 1: "dilatants" exhibit the property in which shear stress increases beyond the increase in shear rate, *i.e.*, $n < 1$; and "thixotropic" flow exhibits the opposite effect, with time dependent

Table 1. The values of the intrinsic viscosities and the Huggins' constants of amylose and amylopectin in dimethylsulfoxide (DMSO) at 25°C

	$[\eta]$	k'
Amylose	0.87 (dl/g)	0.54
Amylopectin	1.22 (dl/g)	2.46

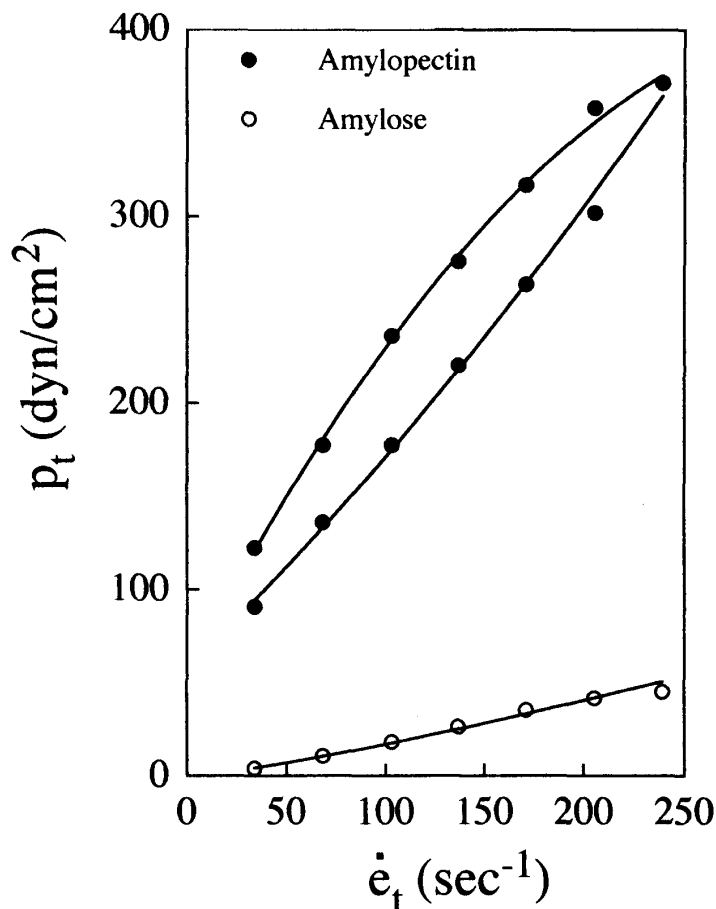


Fig. 2. The relationship between the shear stress and shear rate of 4% amylose and amylopectin in dimethylsulfoxide (DMSO) at 25°C.

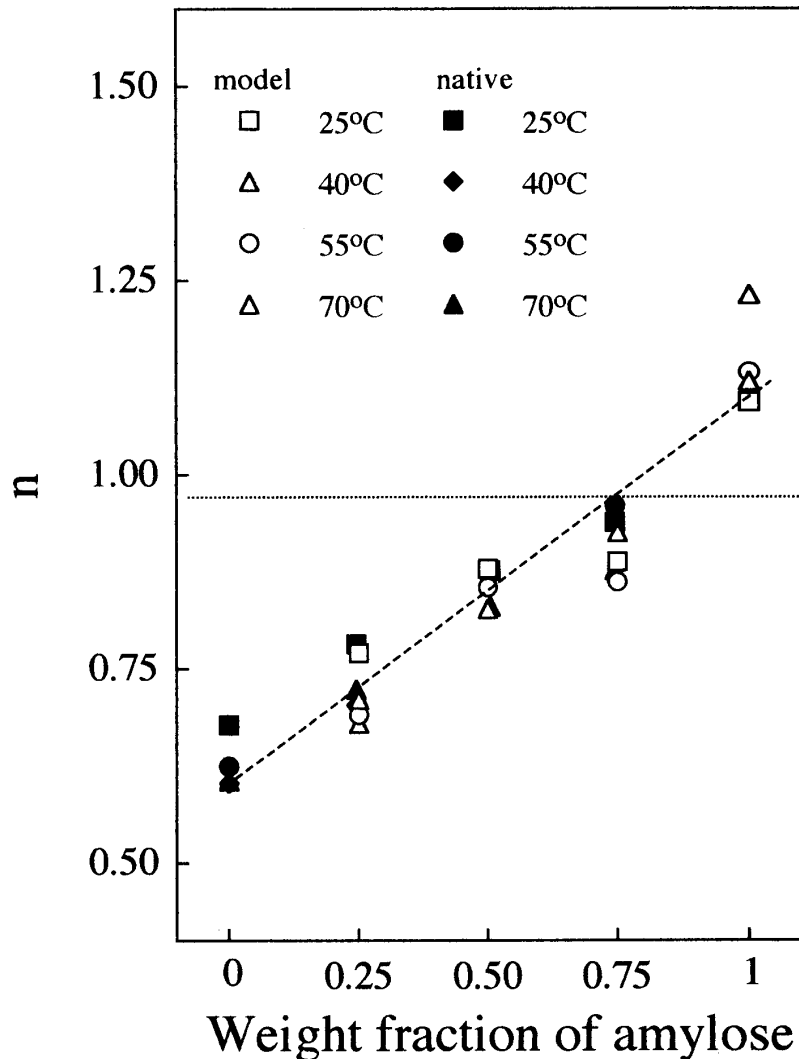


Fig. 3. The relationship between the weight fraction of amylose and the n -values (an index of non-Newtonian flow), estimated using the power law equation, where the concentration of the solution is 5%. In this figure, the term 'model' indicates the mixture of amylose and amylopectin, and the term 'native' indicates corn starch (amylose content of 23%) and the two kinds of high-amylose corn starch (amylose contents of 72% and 51%). The temperature of measurements is sited in the figure.

hysteresis behavior occurring between changes in shear stress and shear rate, *i.e.* $n > 1$. Thus viscosity increases with increasing shear rate in dilatant fluids and decreases with time in thixotropic ones. Thus viscosity of non-Newtonian fluid seems to be an apparent viscosity. The concentrated solutions used in this study could be analyzed using the power law of Eq. (2). Figure 3 shows the relationship between the weight fraction of the amylose or amylopectin and n -values obtained. Although the data in Fig. 3 were obtained from the solution of 5% total sugar concentration, similar results were obtained from solutions of different concentrations. And the model solution, which were prepared in order to coincide with the composition ratio of amylose and amylopectin in the native starch solution. As shown in Fig. 3, it can be seen that the model solutions and the native solution also exhibited non-Newtonian flow in the same way as the solutions of only amylose or amylopectin. The more the

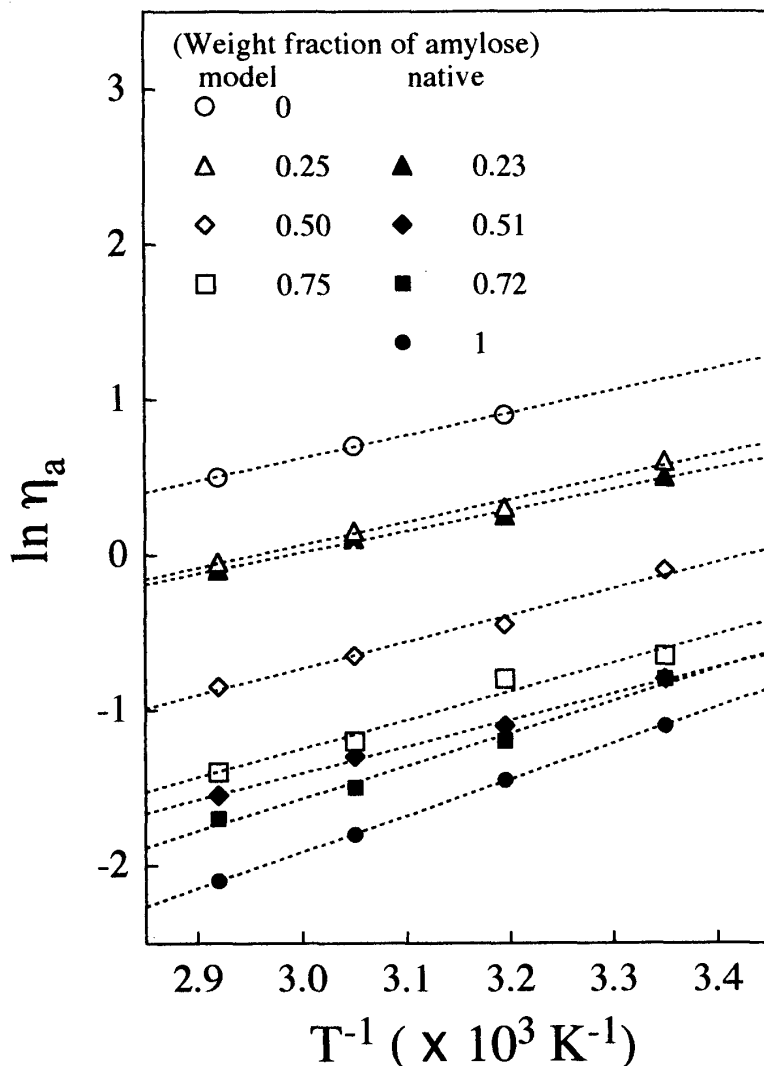


Fig. 4. The plots of logarithm of η_a at shear rate of 240 s^{-1} against the reciprocal of the absolute temperature of 5% starch solutions for a model solution of mixed amylose and amylopectin, and native starch solutions with different amylose contents.

amylose content was increased, the larger the n -values became. Conversely, the more the amylopectin content increased, the smaller the n -value became. The manner of change of the n -values appeared to be linearly dependent upon the ratio of amylose to amylopectin. From the results, it could be said that additivity existed between the flow properties of amylose and amylopectin. On the basis of the n -values obtained, the concentrated amylose solution was found to exhibit dilatancy, $n=0.6$, and the concentrated amylopectin solution showed thixotropic flow, $n=1.25$. The results were considered to be due to the molecular conformation of the loose helix structure of amylose and of the rigid particle structure of amylopectin in solution, respectively. It was also supposed that the amylopectin molecules in the concentrated solutions constructed some special intermolecular structure, because of the heavy interactions suggested by the high value of the Huggins' constant.

Figure 4 shows the plots of the logarithm of apparent viscosity, η_a , at a shear rate of 240 s^{-1} against the reciprocal of the absolute temperature, $1/T$, for native starch solutions and model mixture solutions of 5% concentration. The apparent viscosity of the model mixture solution was greater than

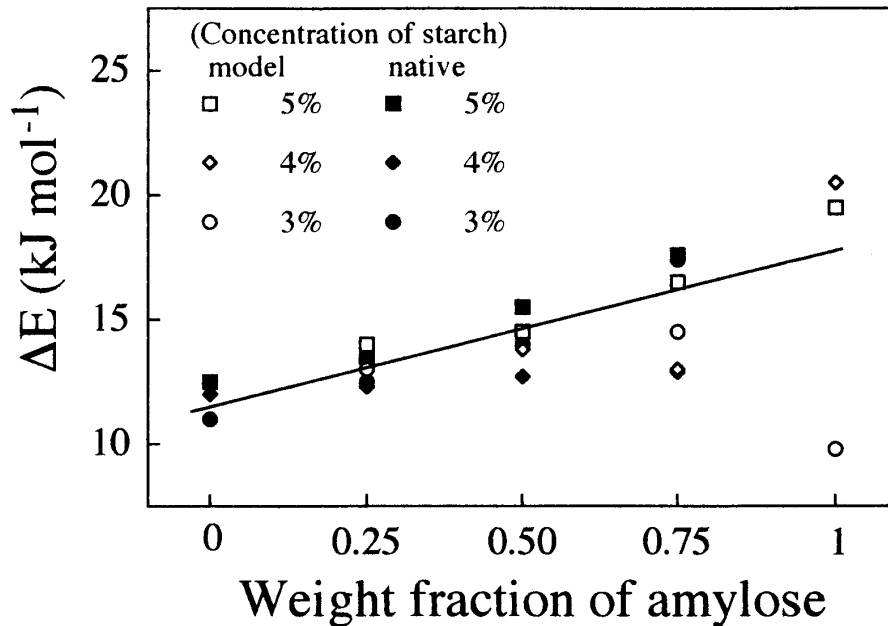


Fig. 5. The relationship between the apparent activation energy of flow and the weight fraction of amylose for a model solution of mixed amylose and amylopectin, and native starch solutions with different amylose contents.

that of the native starch solution, particularly at a high weight fraction of amylose of about 0.5 and 0.7, as shown in Fig. 4. It was considered that native starch granules (which consist of a complex of microcrystal and noncrystal portions) had to first swell in the solvent before dissolving, while the separated amylose and amylopectin were dissolved directly in the solvent. Thus, the lack of sufficient expansion or stretching of the amylose and amylopectin molecules in the native mixture solution resulted in a lower apparent viscosity than that of model mixture solution.

From the slopes of the plots in Fig. 4, the apparent activation energies of flow, ΔE_a , were estimated. The relationship between ΔE_a and the weight fraction of amylose and amylopectin is shown in Fig. 5. As shown in Fig. 5, ΔE_a increases linearly with the increasing amylose fraction. This exhibits the same tendency as the n -values as shown in Fig. 3. It was concluded that the amylose and amylopectin molecules behaved independently in these mixed solutions from the fact that the n -values for both the non-Newtonian index and the ΔE_a showed additivity in relation to the weight fraction of amylose.

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アミロース-アミロペクチン混合溶液の非ニュートン粘性挙動

小川廣男・石毛清美・木尾茂樹・田代有里・磯 直道

デンプン溶液の粘性挙動を明らかにするために、25°Cにおける極限粘度数 $[\eta]$ とハギンス定数 k' とが、それぞれ0.87 dl/g, 0.54のアミロースと、1.22 dl/g, 2.46のアミロペクチンを用いて、その組成比を変化させたときの流動特性を調べた。その結果、アミロース-アミロペクチンの組成比と流動特性および流動の活性化エネルギーは一次の関係を示した。また、各種デンプンの濃厚溶液とそれらのデンプンと同じ組成比に調製したモデル系デンプンの濃厚溶液の流動特性と流動の活性化エネルギーはそれぞれ比較的よい一致を示した。このことから、デンプン濃厚溶液の流動特性および流動の活性化エネルギーにはそれぞれアミロースとアミロペクチン相互の加成性が存在することが明らかとなり、溶液中のアミロースとアミロペクチンはそれぞれ独立に挙動することが示唆された。また、アミロース濃厚溶液が示したダイラタンシー性やアミロペクチン濃厚溶液のチキソトピー性は両分子のコンフォメーションに起因するものと考えた。

キーワード：デンプン，アミロース，アミロペクチン，粘性，非ニュートン流動