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Effect of Reaction Variables on Distribution of Xanthate Groups in Starch Xanthate *

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Introduction

Previous studies at this laboratory have shown that incorporation of crosslinked starch xanthates in paper improves its wet and dry strength considerably (1). Because the potential use of xanthates in this application is large, a rapid, continuous method for xanthating starch was developed (2). Examination of the xanthate thus produced showed that the starch as a whole was uniformly xanthated (3) and that starch xanthates isolated after 1 hour reaction time contained significantly more substitution on primary than on secondary positions (4). ADAMEK and PURVES (3) showed that starch xanthate prepared by an emulsion technique increased in the amount of primary substitution with time.

In view of the reported migration of xanthate groups in viscose (6, 7, 8) the effect of aging on distribution of xanthate groups in starch was examined to provide guidelines for achieving consistent results in subsequent applications. The distribution of xanthate groups between primary and secondary positions was determined by a benzylation-tritylation procedure (4) which was previously found to give results in good agreement with values obtained by a much more time-consuming method involving replacement of xanthate groups with methyl groups, hydrolysis, and subsequent determination of methyl glucoses.

Experimental

Starch Xanthates

Starch xanthate was prepared in a continuous reactor as previously reported (2) using a 1:1:0.5 molar ratio of starch : sodium hydroxide : carbon disulfide to give a theoretical degree of substitution (D.S.) of 0.50. The product discharged from the reactor was a highly viscous material containing 60% solids with D.S. 0.29.

In one experiment the product was collected in 70- to 80-g portions at 30 second intervals, sealed in plastic bags, and stored at 25°C. These samples, after standing for 0, 1, 4, 10, 23, 47, 71 and 144 hours, were dispersed in a Waring Blender with ice and water to give a dispersion of about 2% starch xanthate for reaction with benzyl bromide.

In another experiment the product discharged from the reactor was dispersed immediately in water to 11% starch xanthate concentration in a sigma blade mixer. The dispersion was divided into two parts and stored at 5°C and 20°C. Samples, 300 g of these dispersions were withdrawn after 0, 21, 44, 67, 144, 188, 236, and 332 hours and diluted with ice water to give 2% dispersions for reaction with benzyl bromide.

Benzylation and Tritylation

The method used for preparation of the S-benzyl derivatives of starch xanthate was reported previously (5). The products were recovered in 94–98% of the theoretical yields. Tritylation of the S-benzyl products was carried out as described previously (4). Trityl D.S. was calculated as the average of the values obtained from sulfur analysis, sample weight gain, and yield of triphenyl methanol upon detritylation with sulfuric acid. Unity minus trityl D.S. gave the calculated xanthate D.S. at the primary position.

Results and Discussion

The reaction mass, which was discharged at 50% solids, contained unreacted carbon disulfide and increased in D.S. from an initial 0.29 to 0.44 in 4 hours when allowed to stand in sealed containers at 25°C (Fig. 1).

![Fig. 1. Degree of substitution (D.S.) and distributions in starch xanthates aged at 50% solids and 25°C.](image)

Thereafter, the total D.S. decreased to the initial value in 144 hours. During this interval, portions of the reaction mass were removed periodically and the distribution of xanthate groups between the primary and secondary positions was determined. Analysis of the product soon after discharge showed that 41% of the xanthate groups occupied primary positions and after 4 hours, 57% of the xanthate groups were on primary positions. It is interesting to note that the actual D.S. of xanthate groups on the secondary positions increased only from 0.17 to 0.19 in 4 hours while substitution at the primary position increased from 0.12 to 0.25 during this time. In 24 hours the total D.S. had decreased to 0.40 and 75% of the remaining xanthate groups occupied the primary position at this time. Thereafter, the xanthate D.S. at the secondary positions remained approximately constant and the slow decrease in total D.S. was paralleled by the decrease in D.S. of the primary xanthates.

The increase in total xanthate D.S. was considerably less in the reaction mass diluted to 11% solids. At this dilution, maximum degrees of substitution of only 0.33 and 0.32 were obtained on storage at 5°C (Fig. 2) and 20°C (Fig. 3), respectively. As expected, the rate of deamination was greater at the higher storage temperature. The total D.S. had decreased to 0.16 in 332 hours at 20°C, while at 5°C the D.S. had decreased only to the initial value. Even on prolonged storage for 720 hours at 5°C the D.S. was 0.22. The increase in xanthate substitution at the primary position was
of substituents between the primary and secondary positions.

At 50% solids and 25°C the D.S. increased from 0.29 to a maximum of 0.44 in 4 hours due to the presence of unreacted carbon disulfide in the initial product. The distribution changed from an initial xanthated primary: secondary ratio of 2:3 to an ultimate ratio of 3:1 after 23 hours.

In an 11% aqueous dispersion stored at 5°C and 20°C the starch xanthate of D.S. 0.30 rose to the maximum of 0.33 in 3 days while the primary:secondary ratio changed from an initial 1:5 to a final 1:1 ratio near the D.S. maximum. Thereafter, this latter ratio prevailed during subsequent decomposition of xanthate groups.

Zusammenfassung

Der Substitutionsgrad und die Verteilung der Xanthatgruppen in Stärke-xanthaten auf die primäre und sekundäre Stellung wurde unter Verwendung einer Benzyl­ierung-Tritylierungsmethode ermittelt. Sozusohl die gesamte Xanthatsubstitution als auch die Verteilung der Substituenten auf die primäre und sekundäre Stellung wurden durch Reaktionsbedingungen wie Feststoffgehalt, Temperatur und Zeit beeinflußt.

Bei einem Feststoffgehalt von 30% und einer Temperatur von 25°C stieg der Substitutionsgrad innerhalb von 4 Stunden von 0.29 auf ein Maximum von 0.44 an, was auf die Anwesenheit von unverbrauchtem Schwefel­kohlenstoff im Ausgangsprodukt zurückzuführen ist.Das Verhältnis von primärem zu sekundärem Xanthat betrug anfangs 2:3 und änderte sich im Laufe von 23 Stunden auf einen Endwert von 3:1.

In einer 11%igen wäßrigen Dispersion, die bei 5°C und 20°C gelagert wurde, stieg der Substitutionsgrad des Stärke-xanthates innerhalb von 3 Tagen von 0.30 auf ein Maximum von 0.33, während sich das Verhältnis von primärem zu sekundärem Xanthat von anfänglich 1:5 bis zum Erreichen des Substitutionsmaximums auf 1:1 veränderte. Danach herrschte dieses letzte Ver­hältnis bei fortgesetztem Zerfall von Xanthatgruppen vor.

Résumé

On a déterminé le degré de substitution et la distribution des groupes de xanthate entre les positions primaire et secondaire du xanthate d’amidon à l’aide d’une benzylation-tritylation. Et la substitution totale et la distribution des groupes de xanthate en les positions primaire et secondaire furent influencées par des conditions variables de réaction, comme par exemple la teneur en solides, la température et le temps.

A une teneur en solide de 50% et une température de 25°C, le degré de substitution, en 4 heures, montait de 0,29 à un maximum de 0,44, ce qui est réductible à la présence de soufre de carbone non utilisé dans le produit original. La proportion entre les xanthates primaire et secondaire était au début de 2:3 et changeait en dedans de 23 heures à la cote finale de 3:1.

Dans une dispersion aqueuse de 11% qu’on avait stockée à 5 et à 20°C, le degré de substitution du xanthate d’amidon montait de 0,30 à un maximum de 0,33 en dedans de 3 jours, tandis que la proportion entre les xanthates primaire et secondaire était d’abord de 1:5 et finit par atteindre une cote de 1:1 au maximum de la substitution. Cette dernière proportion prédominait ensuite pendant la décomposition continue des groupes de xanthate.
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