

Specific Interaction of Starch and Polyvinyl Alcohols Having Long Alkyl Groups

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SYNOPSIS

Properties of aqueous solutions of blends of starch and polyvinyl alcohols (PVAs), having alkyl groups as side chains, or at one polymer chain end, were studied in terms of viscosity stability, and transparency. In the case of corn starch, PVAs having butyl, octyl, and dodecyl end groups, as well as PVA copolymers containing small amounts of vinyl versatate, together with itaconic acid, increased the stability of the blended solution. The aqueous solutions of PVA, having dodecyl end groups and oxidized starch blend, also showed good stability in viscosities and considerable increase in transparency, whereas conventional PVA and oxidized starch blend gave turbid aqueous solutions, followed by phase separation. The phenomena were assumed to arise from the interaction of the alkyl group in PVA with starch, forming a helical structure with the alkyl group in the hydrophobic internal part.

INTRODUCTION

Polyvinyl alcohol (PVA) has been utilized together with starch in the fields of warp sizing and paper sizing. Raw starch, such as corn starch, has been produced in large quantities and has been used industrially from the economical point of view, in spite of the retrogradative nature of the aqueous solution. Blends of PVA and starch are incompatible, so that modified starches, such as oxidized starch, are preferred because of a slight improvement of compatibility between both of the polymers.

In the free radical polymerization of vinyl acetate (VAc), it is well known that the reactivity of the propagating radical is so high that chain transfer reactions to the monomer and the polyvinyl acetate (PVAc) occur significantly. The propagating radical abstracts a hydrogen atom from acetyl groups of PVAc, so that a long branch is introduced into the polymer by successive addition of the monomer to the newly formed radical.¹ The long branch, thus formed, is broken in the course of alkaline hydrolysis to PVA, yielding an end group of sodium carboxylate

or a lactone ring formed by the reaction of the carboxyl group with the hydroxyl group in an adjacent monomer unit.^{1,2}

In the presence of a solvent or a chain transfer agent for the polymerization, a chain transfer reaction from the propagating radical to the solvent or the chain transfer agent also occurs resulting in the formation of PVAc, having the solvent or the chain transfer moiety at one polymer end, from which PVA, having the same end group, can easily be derived. The authors have studied and developed new kinds of PVAs, having a variety of chain transfer agents at one end, using mercaptans as chain transfer agents in the polymerization of VAc, followed by the usual alkaline hydrolysis in methanol.³⁻⁷

Among these end-group modified PVAs, those having long alkyl end groups have been found to exhibit specific interaction with starch.^{8,9}

Long alkyl side groups can easily be introduced to PVAc by copolymerizing VAc with small amounts of comonomers, having long alkyl groups. In this case, however, attention is needed to avoid the scission of the alkyl groups in the course of alkaline hydrolysis to PVA. Vinyl ethers, having long alkyl groups, and vinyl esters of tert-carboxylic acid, having long alkyl groups, are preferable in this regard.

In this article the interaction of the PVAs, having

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long alkyl groups either as side chains or at one end, with corn starch, as well as interactions of the PVA, having long alkyl end groups with oxidized starch, will be reported.

EXPERIMENTAL

Samples

The conventional PVA was of commercial grade POVAL 105 (Kuraray Co., Ltd., DP 550), which was extracted in a Soxhlet apparatus with methanol so as to remove sodium acetate. The samples of PVA, having alkyl end groups, were synthesized by free radical polymerization of VAc using azo-bis-isobutyronitrile as an initiator at 60°C in the presence of corresponding alkyl mercaptans as chain transfer agents. The alkyl mercaptans were added continuously, as polymer conversion increased, to keep the concentration ratio of mercaptans to VAc constant so as to obtain PVA with a narrow molecular weight distribution, followed by usual alkaline hydrolysis in methanol. The blocking efficiency, which is defined as the ratio of the PVA molecules having a chain transfer moiety at one end to total PVA molecules, increases with a decrease in DP.¹⁰ The values were estimated to be 0.81 and 0.96 for two samples of DP 560 and 120, respectively. (A detailed study with NMR end group analysis will be reported elsewhere.¹¹) The PVA having a C_nH_{2n+1} end group is expressed as C_nH_{2n+1} -PVA.

Copolymers of PVA were synthesized by copolymerizing VAc with corresponding comonomers, followed by the usual alkaline hydrolysis. Special care was paid to equalize the copolymer composition by supplying the acid comonomers continuously when the monomer reactivity ratios were much different from each other, such as the systems of VAc and itaconic acid and of VAc and maleic anhydride. Vinyl versatate (the vinyl ester of C_{10} tert-carboxylic acid mixture, Shell Fine Chemicals), of commercial grade, was selected because alkyl ester side chains are stable to alkaline hydrolysis. The degrees of hydrolysis of PVAs (DH) were 99%, unless otherwise mentioned.

Corn starch was used as obtained. Oxidized starch was of commercial grade (Mermaid M-200, Matsumoto Yushi-Seiyaku Co., Ltd.). High amylose content starch (Honen Oil Co., Ltd.), which is a kind of special corn starch containing 70% amylose, was used as obtained. Amylopectin was used after separation of amylose from corn starch by adding *n*-butanol to the aqueous solution to form the pre-

cipitated *n*-butanol-amylose complex,¹² which was removed by filtration.

Measurement

Viscosities of aqueous solutions were measured using a Brookfield BL-type viscometer. In the case of the measurement of high viscosity solutions, where the samples were thought to show non-Newtonian flow, the following rotor numbers were used at 30 rpm: viscosity range 200–800 cp, rotor number 2; viscosity range 800–4000 cp, rotor number 3; viscosity range > 4000 cp, rotor number 4.

In the spectroscopic measurements, transmittance of aqueous solutions was measured at 20°C using 1 cm cell length at the wavelength of 650 nm.

The degrees of polymerization (DP) of PVAs were determined viscometrically in acetone solutions of the polyvinyl acetates in order to avoid overestimation caused by hydrophobic interaction between alkyl groups in aqueous solution,¹⁰ by using Nakajima's relationship¹³ as follows:

$$[\eta] = 7.94 \times 10^{-3} DP^{0.62} \text{ (in dL/g, at } 30^\circ\text{C)}$$

RESULTS

Aqueous Solution Viscosities of Blends of Corn Starch and Various Types of PVA

Various types of PVA, having long alkyl groups either as side chains or at a chain end, were dissolved with equal amounts of corn starch at 95°C, and their viscosities were measured at 90°C, 20°C, and at 20°C after 1 day storage, as shown in Table I.

The aqueous solution of a conventional PVA-corn starch blend showed phase separation after 1 day storage. The PVAs, having butyl or dodecyl groups at one end, formed stable aqueous solution with corn starch, whereas the blend composed of corn starch and the PVA, having an octyl group at one end, showed less stability after one day storage. However, this is not thought to be an unexpected phenomenon, since the degree of hydrolysis of the PVA having an octyl end group was so high (>99.9%) that the aqueous solution of the PVA itself became gelled because of enhanced crystallizability in water, which is the well-known nature of fully hydrolyzed PVA.^{14,15} In the case of the PVA having an octadecyl group at one end, the aqueous solution of the blend showed phase separation after one day storage. However, introduction of a small number of carboxylic groups into the side chains of PVA,

Table I Viscosities of Aqueous Blends of Corn Starch and Various PVAs (Corn Starch/PVA: 1/1; Concentration of Polymers; 5%; Solubilization Temperature: 95°C)

PVA	Viscosity (cp)		
	90°C	20°C	20°C after 1 Day
Conventional PVA (DP = 550)	9	110	Phase Separation
VV-co-PVA ^a (DP = 800)	15	227	540
SVE-co-PVA ^b (DP = 1700)	370	2620 (gelled)	
LVE-co-PVA ^c (DP = 1700)	210	6370 (gelled)	
C ₄ H ₉ -PVA (DP = 78)	24	80	330
C ₈ H ₁₇ -PVA ^d (DP = 88)	81	1120	3260 (gelled)
C ₁₂ H ₂₅ -PVA (DP = 120)	113	640	710
C ₁₈ H ₃₆ -PVA (DP = 159)	2	6	Phase Separation
Man-co-C ₁₈ H ₃₇ -PVA ^e (DP = 100)	100	1380	2850

^a 3 mol % vinyl versatate and 1 mol % itaconic acid copolymerized.

^b 0.3 mol % octadecyl vinyl ether copolymerized.

^c 0.6 mol % dodecyl vinyl ether copolymerized.

^d DH being higher than 99.9%.

^e 3 mol % maleic anhydride copolymerized.

having an octadecyl end group by copolymerization with maleic anhydride, the ring of which is opened to form carboxylic groups in the course of alkaline hydrolysis, increased the aqueous solution stability to some extent. Among the tested PVA copolymers, having alkyl groups as side chains, the copolymer containing vinyl versatate together with itaconic

acid exhibited stable aqueous solution formation with corn starch. However, the copolymer containing octadecyl vinyl ether or dodecyl vinyl ether did not exhibit stable aqueous solution formation with corn starch, although there existed some kind of interaction, as judged from the fact that gelation after cooling to 20°C occurred without phase separation.

Table II Viscosities of Aqueous Solutions of Blends of Corn Starch and PVAs

PVA	(Wt %)	Concentration of Polymers (Wt %)	Viscosity (cp)			Viscosity Ratio	
			90°C (A)	20°C (B)	20°C After 1 Day (C)	(B/A)	(C/B)
C ₁₂ H ₂₅ -PVA (DP = 120)	0	5.0	7.0	625	2020	89	3.2
	10	5.1	7.5	300	400	40	1.3
	20	5.1	6.5	2570	3100	395	1.2
	30	5.3	6.2	2390	3080	384	1.3
	50	5.0	5.0	440	610	86	1.4
	70	5.2	2.1	13	13	6.2	1.0
	100	5.0	1.6	5.7	—	—	—
C ₁₂ H ₂₅ -PVA (DP = 560)	10	5.1	7.4	87	560	11.8	6.4
	20	5.3	7.5	55	65	7.3	1.2
	30	5.4	7.6	42	41	5.5	1.0
	50	5.6	8.0	67	71	8.4	1.1
	100	5.0	3.9	25	—	—	—
Conventional-PVA (DP = 550)	10	5.7	7.0	370	1490	53	4.0
	20	5.2	6.5	76	960	11.7	12.7
	70	4.9	2.6	12	11	4.6	0.9
	100	5.0	2.0	7.7	—	—	—

Behavior of Aqueous Solutions of Blends of Corn Starch with the PVA, Having a Dodecyl End Group

Corn Starch was gelatinized at 125°C and was mixed at various ratios with an aqueous solution of PVA, having a dodecyl end group at 95°C. The concentration of the total of both polymers was kept constant at 5%. The viscosities of the aqueous solutions of the blends were measured at 90°C and 20°C, and at 20°C after 1 day storage. Table II shows the results, where PVAs having dodecyl end groups of DP 120 and 560, as well as conventional PVA of DP 550, were tested.

As is clear from Table II, there seemed to exist almost no specific behavior in the viscosities of the aqueous solutions of the blends measured at 90°C. On the other hand, the viscosities at 20°C, both immediately after cooling and after 1 day storage, exhibited obvious abnormalities. To make the phenomenon clearer, the ratios of viscosities at 20°C to those at 90°C, as well as viscosities at 20°C after 1 day storage to those just after cooling to 20°C, were plotted against weight fraction of the PVA in the mixture, in Figures 1 and 2, respectively.

In the absence of PVA, aqueous solution viscosity of corn starch increased on cooling and also on storage, due to well-known retrogradation. In the presence of conventional PVA, the blend solutions were turbid and phase separation took place on cooling to 20°C, showing incompatibility. On the contrary, in the presence of PVA having dodecyl end groups,

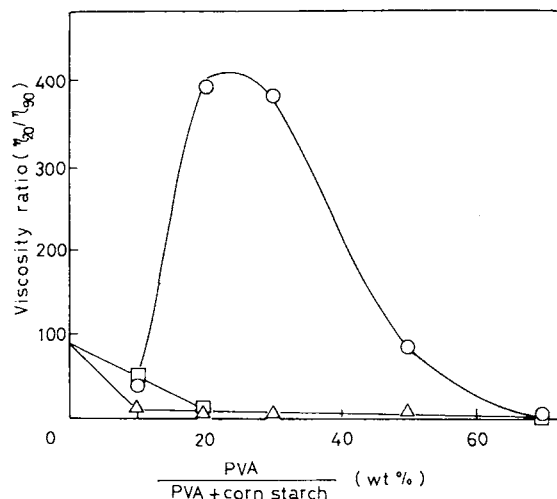


Figure 1 Relationship between PVA fraction in PVA-corn starch blends and ratio of aqueous solution viscosities at 20°C and at 90°C. PVA + corn starch: 5%; Solubilizing temperature: 125°C for corn starch, 95°C for PVA. (○) C₁₂H₂₅-PVA (DP = 120), (△) C₁₂H₂₅-PVA (DP = 560), (□) Conventional PVA (DP = 550).

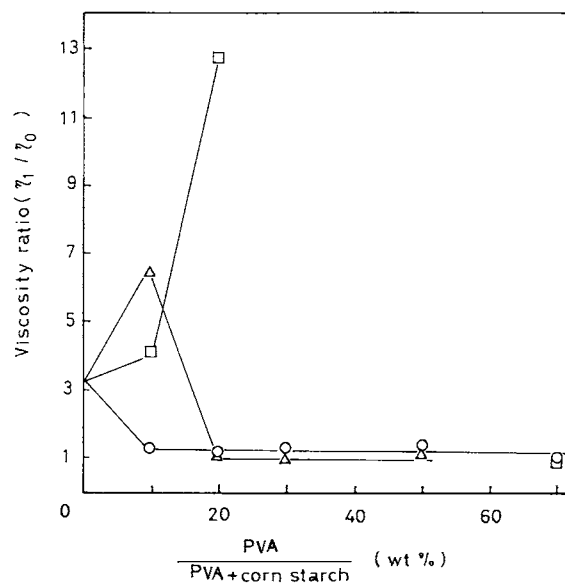


Figure 2 Change in viscosities of aqueous solutions of PVA-corn starch blends after 1 day storage at 20°C. η_1 : Viscosity after 1 day; η_0 : Viscosity after cooling; Viscosity measurement: 20°C; PVA + corn starch: 5%; Solubilizing temperature: 125°C for corn starch, 95°C for PVA. (○) C₁₂H₂₅-PVA (DP = 120), (△) C₁₂H₂₅-PVA (DP = 560), (□) Conventional PVA (DP = 550).

the viscosity behavior was different, as follows: In the case of lower degrees of polymerization (DP = 120), the viscosities of aqueous solutions of blends, after cooling to 20°C, increased to a great extent with increases in the PVA fraction from 20 to 50% and the viscosity increases after 1 day storage were much smaller compared with a conventional PVA blend system. In the case of higher molecular weight PVA (DP = 560), the viscosities of aqueous solutions of blends after cooling to 20°C were low and the viscosity increases after 1 day storage were not observed, except at the lowest PVA content of 10%. The transparency and stability of the aqueous solution of the blend of corn starch and the PVA having dodecyl end groups showed much improvement as compared with the conventional PVA system. These results seem to suggest that the PVA with dodecyl end groups becomes compatible with corn starch in aqueous solution.

Behavior of Aqueous Solutions of Blends of Oxidized Starch with the PVA Having Dodecyl End Groups

Aqueous solution blends with PVA having dodecyl end groups and oxidized starch instead of corn starch were studied in detail. The viscosities of aqueous solutions of these blends, as well as blends with the

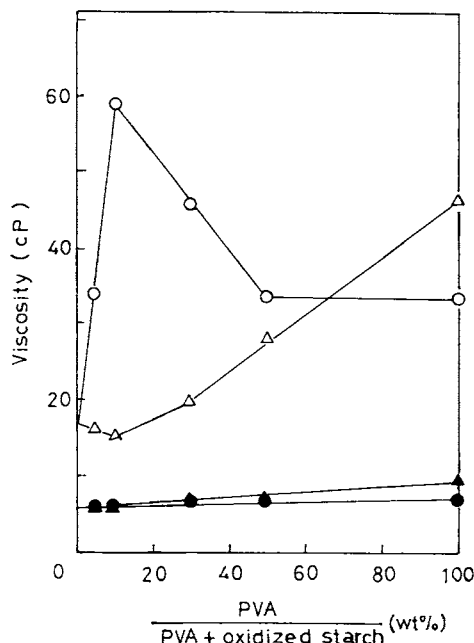


Figure 3 Aqueous solution viscosities of PVA-oxidized starch blend plotted against PVA fraction. Solubilizing temperature: 95°C; PVA + oxidized starch: 10%; (○), (●) $C_{12}H_{25}$ -PVA (DP = 135); (△), (▲) Conventional PVA (DP = 550); Open mark: measured at 20°C; Solid mark: measured at 90°C.

conventional PVA system, are shown in Figure 3. Polymer concentration was 10 wt % and solubilization was carried out at 95°C.

The aqueous solution of the conventional PVA with oxidized starch showed a typical, incompatible curve at 20°C, unlike that of the PVA having dodecyl groups with oxidized starch, which exhibited abnormality thought to be due to the existence of specific interactions between both polymers. In both cases, it was not clear whether there existed a specific interaction in the aqueous solution at 90°C.

The viscosity changes in the aqueous solutions of the blends during storage at 20°C are shown in Figure 4. The aqueous solution of oxidized starch itself reached constant viscosity after a slight increase during 3 days. In the case of the conventional PVA and oxidized starch system, equal amounts in the blend led to phase separation and the 30/70 blend showed almost constant viscosity. In the case of the PVA having dodecyl end groups and an oxidized starch system, the 10/90 and 30/70 blends reached almost constant viscosities after increasing to some extent up to 3 days. On the other hand, there were viscosity increases in aqueous solutions of the conventional PVA and those of the PVA having dodecyl end groups. Since the increase in aqueous solution viscosity of PVA, especially when a high degree of

hydrolysis is involved, is well-known,^{14,15} our results must be attributed to the nature of PVA. The viscosity increase, observed in the case of equal amounts in the blend of the PVA having dodecyl end groups and oxidized starch, might be attributed to the nature of the PVA.

The transmittance of the PVA and oxidized starch solution obtained above are shown in Figure 5. While the transmittance of the aqueous solutions of blends of conventional PVA and oxidized starch were extremely low in the region of the weight ratios from 5/95 to 50/50, those of the PVA having dodecyl end group and oxidized starch were high, showing improvement in compatibility, although there did exist low transparency with low levels of the PVA. The changes in the transmittance during storage at 20°C are shown in Figure 6. In summary, the transmittance did not change substantially, with the exception of the solutions of the PVA having dodecyl end groups and its 50/50 blend with oxidized starch. This might be attributed to the same gelation phenomena mentioned above. The cooling method

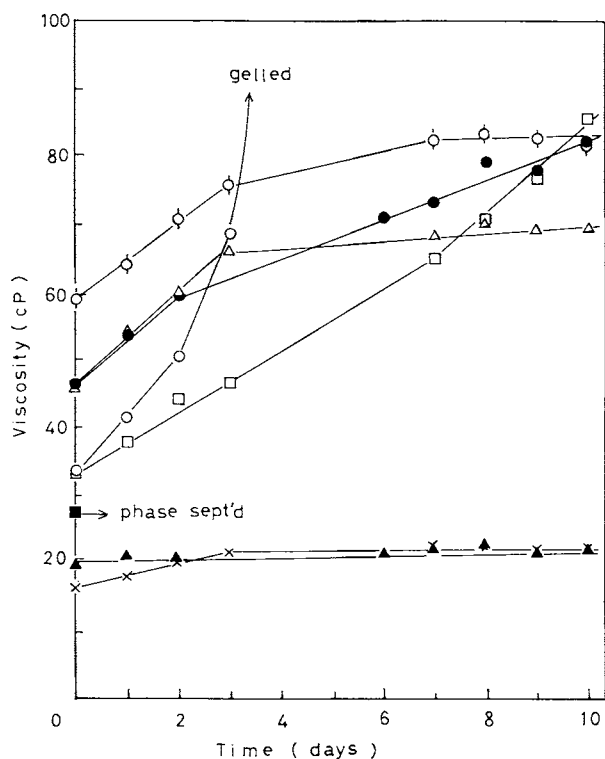


Figure 4 Change in viscosities of aqueous solutions of PVA-oxidized starch blends on storage at 20°C. Solubilizing temperature: 95°C; PVA + oxidized starch: 10%; Weight ratio of conventional PVA to oxidized starch: (●) 100/0, (■) 50/50, (▲) 30/70, (×) 0/100. Weight ratio of $C_{12}H_{25}$ -PVA (DP = 135) to oxidized starch: (○) 100/0, (□) 50/50, (△) 30/70 (◐) 10/90.

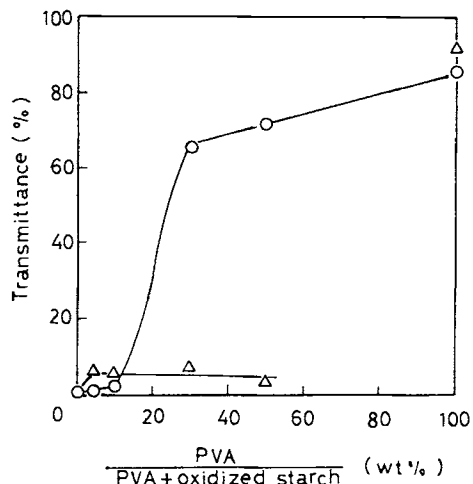


Figure 5 Relationship between transmittance of the aqueous solutions and weight fraction of PVA in PVA-oxidized starch blends. PVA + oxidized starch: 10%, Solubilizing temperature: 95°C, (O) $C_{12}H_{25}$ -PVA/oxidized starch, (Δ) conventional PVA/oxidized starch.

after solubilization was the same for these experiments, that is, the vessel was left at 20°C in air.

Since different behavior was observed depending upon the cooling speed, especially with low ratios of PVA to oxidized starch, we carried out two kinds of cooling: one was gradual cooling as usual, and the other was quenching in water bath. Figure 7 shows that the transmittance of the aqueous solution of the oxidized starch itself, as well as that of the PVA-oxidized starch blends, was affected considerably by cooling speed. In the case of the PVA, having dodecyl end groups with a lower degree of polymerization (DP = 200), the addition of more than 3 parts of the PVA to 100 parts of the oxidized starch gave a clear solution under the quenching condition, whereas under gradual cooling no such effect was observed at less than 5 parts addition. To the contrary, in the case of the PVA having dodecyl end groups with a higher degree of polymerization (DP = 560), the addition of up to 7 parts of the PVA to 100 parts of the oxidized starch did not give a clear solution under the quenching method. However, when 20 parts of the latter PVA was added to 100 parts of the oxidized starch using the quenching method, the transmittance was observed to increase to more than 50%, although the result is not shown in Figure 7.

DISCUSSION

Specific interaction between those PVAs, having long alkyl groups as side chains or at one end, and

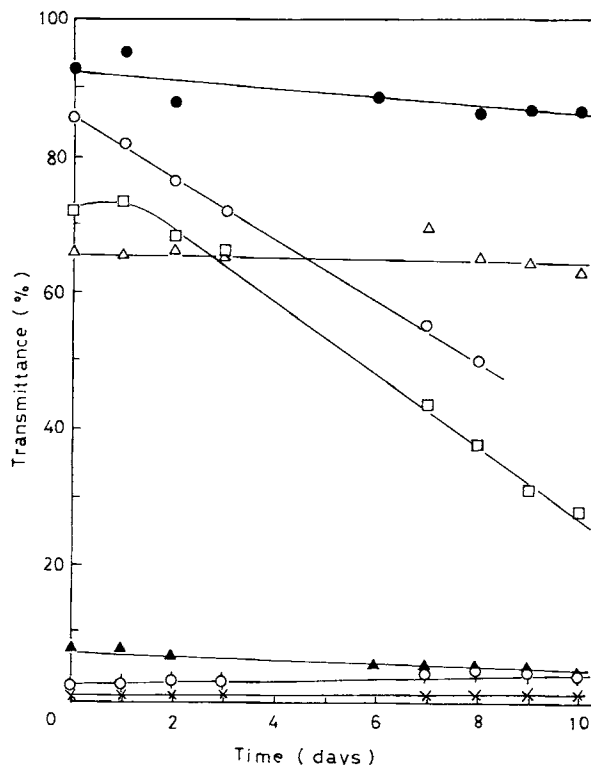


Figure 6 Change in transmittance of the aqueous solutions of PVA-oxidized starch blends on storage at 20°C. PVA + oxidized starch: 10%, Solubilizing temperature: 95°C, Weight ratio of conventional PVA to oxidized starch; (\bullet) 100/0, (\blacktriangle) 30/70, Weight ratio of $C_{12}H_{25}$ -PVA (DP = 135) to oxidized starch; (O) 100/0, (\square) 50/50, (Δ) 30/70, (\odot) 10/90, (\times) 0/100.

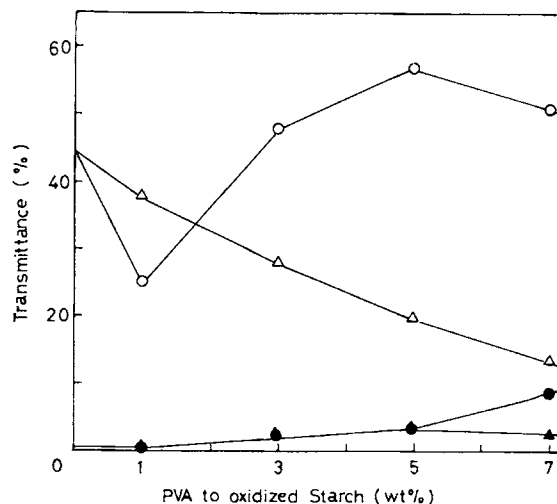


Figure 7 Effect of cooling method to 20°C on transmittance of the aqueous solutions of PVA-oxidized starch blends. Solubilizing temperature: 95°C, Concentration of oxidized starch: Constant (10 wt %), Concentration of PVA varied; (O), (\bullet) $C_{12}H_{25}$ -PVA (DP = 200); (Δ), (\blacktriangle) $C_{12}H_{25}$ -PVA (DP = 560); Open mark: Quenching; Solid mark: Gradual cooling.

starch in aqueous solution were shown in several cases. PVA, having alkyl end groups, exhibited especially interesting behavior, such as an increase in viscosity after cooling, inhibition of increased viscosity on storage, and a remarkable improvement in transparency in blends with oxidized starch. Although the authors do not have clear evidence yet, these effects might arise from the interaction of the long alkyl groups in the PVA with amylose or amylopectin in starch, resulting in the formation of a helix including alkyl groups in the hydrophobic internal part. This has been reported between starch with *n*-butanol, surfactants, and so forth.^{12,16,17} After the helix is formed, the PVA is physically bound to amylose or amylopectin, leading to the improvement in compatibility between both polymers.

In the case of PVA copolymers with alkyl side chains, the PVA having versatic side groups, together with carboxylic acid groups, showed a specific interaction with corn starch in aqueous solution. This might be attributed to sufficient ratios of the alkyl groups to vinyl alcohol units (one alkyl unit to 30 vinyl alcohol units), in comparison with PVA copolymers having octadecyl and dodecyl side groups (one alkyl unit to 330 and 170 vinyl alcohol units, respectively). This suggests weak interaction with corn starch in aqueous solutions for the latter ratio. In addition to this, carboxylic acid groups in the former copolymer might contribute to the stability, since the acid groups increase the stability of the aqueous solution blend of the PVA having octadecyl

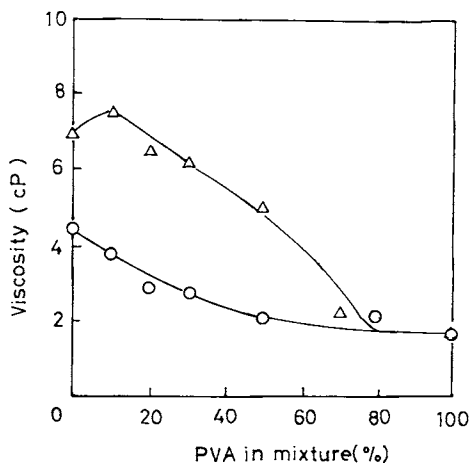


Figure 8 Aqueous solution viscosities of PVA having dodecyl end group and high amylose starch blend in comparison with the PVA and corn starch blend. Solubilizing temperature: 125°C for starch, 95°C for PVA; Total polymer content: 5%, Viscosity measurement: 90°C, PVA: C₁₂H₂₅-PVA (DP = 120), (O) High amylose blend, (Δ) Corn starch blend.

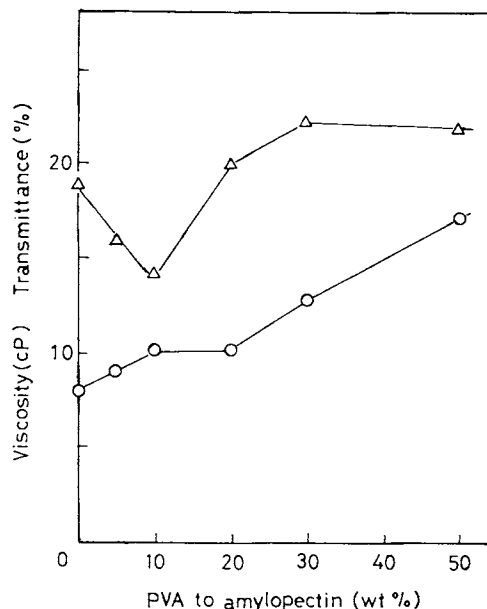


Figure 9 Properties of aqueous solutions of PVA having dodecyl end group and amylopectin blends. (O) Viscosity at 20°C, (Δ) Transmittance at 20°C, Solubilizing temperature: 95°C, Concentration of amylopectin: Constant (10 wt %), Concentration of the PVA: Varied, PVA: C₁₂H₂₅-PVA (DP = 200).

end groups with corn starch to some extent. There might exist increased ability for interaction of alkyl end groups with starch than for alkyl side chains with starch.

In relation to the alkyl group content mentioned above, the PVA having dodecyl end groups exhibited a rather strong effect of degree of polymerization on viscosities and transparency in the case of aqueous solutions with starch, as shown in Table II and Figure 7.

To clarify which is the main species, amylose or amylopectin, causing the specific interaction with PVA having dodecyl end groups, aqueous solution viscosities of blends were measured using high amylose starch and amylopectin, respectively. Figure 8 shows the aqueous solution viscosities, at 90°C, of the blends of high amylose starch (amylose content 70%) and the PVA in comparison with those of the corn starch and the PVA listed in the Table II. The high amylose starch was gelatinized at 125°C and was mixed with aqueous solution of the PVA at 95°C. Figure 9 shows the viscosity at 20°C and transmittance of the aqueous blends of amylopectin and the PVA solubilized simultaneously at 95°C.

As is clear in Figure 8, the two curves showing the relation between the viscosity and weight fraction of PVA in mixtures with high amylose or corn starch indicate different trends, that is, the convex

curve for the corn starch mixture and the concave one for the high amylose starch mixture. This seems to indicate that amylose is not the species that is compatible with the PVA having dodecyl end groups. On the other hand, the addition of small amounts of the PVA having dodecyl end groups to the amylopectin aqueous solution gave characteristic curves in viscosity and in transparency, showing possible interaction. This seems to indicate that amylopectin may be the species compatible with the PVA having dodecyl end groups.

Gudmundsson and Eliasson¹⁸ reported an interesting and similar result recently in the case of complex formation of starch with surfactants that have long alkyl groups. They concluded that amylopectin is the active species, rather than amylose, in the complex formation of surfactants with starch, by the study of thermograms and X-ray diffraction analysis. However, more detailed study using higher purified amylose and amylopectin will be required to clarify the specific interaction of the PVAs having long alkyl groups with starch.

CONCLUSIONS

The PVAs having long alkyl groups, either as a side chain or at one end, cause improvement in compatibility with corn starch and oxidized starch in aqueous solution. This effect is thought to arise from the interaction between alkyl groups in the PVAs and starch, forming a helical structure with the alkyl group in the hydrophobic internal part, where amylopectin rather than amylose might play a more important role. The complex formation might contribute to retardation of retrogradation of starch and to increased compatibility.

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