

Graft Polymerization of Vinyl Acetate Onto Granular Starch: Comparison on the Potassium Persulfate and Ceric Ammonium Nitrate Initiated System

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ABSTRACT: This work was undertaken to discuss in depth the vital differences in the morphological development during synthesis, and properties of starch-g-poly(vinyl acetate) copolymers using two different initiators, potassium persulfate (KPS) and ceric ammonium nitrate (CAN). KPS-initiated system gave relatively low values of grafting ratio and grafting efficiency, indicating a great tendency for the formation of poly(vinyl acetate) homopolymer (PVAc). Yet, higher values were seen for the CAN-initiated system. Transmission electron microscope observations indicated a relatively broad distribution of latex particles for the KPS-initiated system. The surface potential of latex particles was about -3.5 mV, which turned out to be insufficient to maintain stability of latex particles. On the other hand, a uniform particle size distribution was found for the CAN-initiated system, as the surface poten-

tial of latex particles was 21.5 mV. Moreover, radicals on starch molecules were generated directly through a redox reaction with positively charged ceric ion. The hydrophobic PVAc chains were thus grafted on starch, resulting in an amphiphilic graft copolymer, which provides a sufficient stabilization degree as a role of surfactant to render a relatively uniform distribution of latex particles. The synthesized starch-g-poly(vinyl acetate) copolymers were further converted to starch-g-poly(vinyl alcohol) through saponification, which were subjected to evaluations regarding the biodegradation and cell culture capability. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3017–3027, 2006

Key words: potassium persulfate; ceric ammonium nitrate; starch; graft copolymers

INTRODUCTION

Biodegradable polymers featuring ecological advantage toward sustainable development have been of great commercial interest because of a growing environmental concern.¹ In particular, materials containing biopolymer fillers derived from annually renewable resources have received much attention recently. Starch, one of the most abundant natural food sources from most plants, has been considered as attractive biopolymer filler because of its low cost, low density, nonabrasive nature, and biodegradability. Griffin in 1975 pioneered to blend granular starch with plastic materials.² Unfortunately, native starch generally exists in a granular state owing to the in-

herent hydrogen bonding between adjacent molecules. This in turn fails to disperse starch in an extreme fine scale of size into the plastic matrix. Efforts to cope with this problem have led to a recent development of thermoplastic starch prepared by incorporating suitable amounts of water and/or plasticizers, termed “gelatinization.”³ Grafting of matrix resin onto starch molecule also paves another way to resolve this encountered difficulty. In addition, starch grafted copolymer not only can be directly used as a compatibilizer, but also simply served as neat thermoplastics for targeted applications. Thus, numerous works have been investigated regarding the methods of graft copolymerization, such as potassium persulfate (KPS),⁴ ceric ion,^{5–7} and ferrous ion.⁸

Hebeish et al.⁴ has investigated the graft copolymerization of methacrylic acid onto maize starch using a KPS/sodium thiosulfate redox initiation system. Several major factors affecting the graft reaction, such as the state of starch, redox ratio of the initiator, monomer and initiator concentrations, reaction time and temperature, have been discussed. It

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was found that starch-g-poly(methacrylic acid) copolymer was the main product only when starch was preswelled or gelatinized prior to graft reaction to minimize homopolymer formation. Using ceric ammonium nitrate (CAN) initiator, graft copolymerization of methyl acrylate onto potato starch has been carried out by Liu et al.⁵ Several reaction variables were investigated to obtain the optimum reaction condition having the highest grafting efficiency and grafting percentage. In an effort to further elucidate the detail mechanisms of redox initiation systems, Trimnell et al.⁶ has compared the effect of two different initiators, ferrous ammonium sulfate/hydrogen peroxide (FAS/H₂O₂) and CAN, respectively, for the graft copolymerization of methyl acrylate onto granular corn starch. Significant amounts of polymethacrylate homopolymer were observed for FAS/H₂O₂ but not for CAN initiation because of a difference in forming starch macroradicals. Deshmukh et al.⁹ have used CAN initiator to graft acrylamide onto a starch and a modified-cellulose. They have concluded that the increase of CAN concentration would increase the number of grafted chains, yet with shorter chain length. As the concentration of monomer increased, the length of grafted polyacrylamide chains increased.

Though those aforementioned starch graft copolymerization systems have been carried out to impart starch with different functionalities and performances, the biodegradability of resulting graft copolymer normally was rather limited unfortunately. To further resolve this difficulty, some works have been focused on the graft copolymerization of vinyl acetate (VAc) onto starch followed by a saponification to form starch-g-poly(vinyl alcohol) (starch-g-PVOH) known for its complete biodegradability.^{7,8,10} However, the effects of reaction variables on the morphological development during synthesis and properties of the resulted graft copolymers have not been well discussed. This work was therefore undertaken to discuss in depth the vital differences in the structural characteristics and properties for resulting copolymers initiated with KPS and CAN, respectively.

EXPERIMENTAL

Materials

The materials used for graft reaction were VAc, corn starch, KPS, and CAN. VAc monomer was supplied from Lancaster (Morecambe, England) and was purified through distillation. Corn starch and two initiators, KPS and CAN, were all purchased from Nacalai Tesque (Kyoto, Japan). Sodium Hydroxide (NaOH) from Aldrich (Milwaukee, WI) was used for alcoholysis of PVAc to PVOH. α -Amylase obtained from Merck (Darmstadt, Germany) was used for the evaluation of biodegradability. Potassium dihydrogen

phosphate (KH₂PO₄) and disodium hydrogen phosphate (Na₂KHPO₄) to prepare a phosphate buffer solution were received from Showa (Tokyo, Japan) and Acros (Belgium), respectively. A mixture prepared from Dulbecco's modified Eagle's medium (DMEM) from Gibco Company (USA) with 10% of fetal bovine serum (FBS) and 1% of antibiotics was used as the cell culture medium.

Graft copolymerization

Graft copolymerization of VAc onto corn starch was carried out in a typical four-necked flask equipped with a two-blade paddle-type impeller. Starch (30 g) was gelatinized in water (870 mL) for 1 h under 90°C and then the solution was cooled down for further reaction. After the addition of 30 mL of aqueous solution containing 0.018 mol of initiator, various amounts of VAc (15, 30, and 60 g) were then incorporated to perform graft reaction under two different initiated systems of KPS and CAN for 3 h at 50°C. Conversion (%) was determined by the gravimetric method of solid product precipitated from 25 mL of sample solution by the addition of ethanol nonsolvent and hydroquinone for inhibiting further radical polymerization, followed by a vacuum drying at 50°C to a constant weight. PVAc homopolymer, if any, was further extracted from the precipitated product with acetone through Soxhlet extractor for 72 h and weighed for the evaluation of grafting efficiency (GE, %) and grafting ratio (GR). The following denotations are used in this study,

$$\text{Conversion (\%)} = \frac{\text{wt. of grafted and ungrafted PVAc}}{\text{wt. of VAc feed}}$$

$$\begin{aligned} \text{Grafting efficiency (\%)} \\ = \frac{\text{wt. of grafted PVAc}}{\text{wt. of grafted and ungrafted PVAc}} \end{aligned}$$

$$\text{Grafting ratio} = \frac{\text{wt. of grafted PVAc}}{\text{wt. of starch}}$$

After a complete reaction, the mixture solution including graft copolymer and homopolymer was subjected to a dialysis to remove residual monomer and initiators for 7 days. The PVAc portion of obtained dialysis product was further converted to PVOH by saponification. Twenty grams of NaOH was added into a 20 mL of deionized water, which was then mixed with 500 mL of methanol at 40°C. The prepared dialysis solution was added dropwise with a total amount of 250 mL in 40 min followed by another 20 min for a complete alcoholysis. Final product, starch-g-PVOH/PVOH, was filtrated and neutralized with methanol/water (1 : 1) for further evaluation. In general, samples for characterization

and properties evaluation were prepared by oven-drying. The sample solution was poured into a mold and dried in an oven at 50°C for 24 h. It was followed by further drying in a vacuum oven at 50°C for another 24 h.

Characterizations

The zeta potential of latex particles taken immediately after the end of experiment was determined using a Zetamaster (Malvern). Each emulsion was diluted until the solid content reached $\sim 0.005\%$. The reported zeta potential represents an average of five measurements. The Infrared spectra for graft copolymer were recorded on a Spectrophotometer (Perkin-Elmer, Spectrum One) at a resolution of 4 cm^{-1} for 32 scans from 4000 to 400 cm^{-1} . Molecular weight of pure PVAc or grafted PVAc separated from acid hydrolysis of starch on the graft copolymer was determined with a gel permeation chromatography (Waters 510) and calibrated with six different PS standards. The eluent solvent was tetrahydrofuran (THF) and the flow rate was 1 mL/min . Glass transition temperature (T_g) and melt temperature (T_m) of samples were measured using a DSC (TA, TA 2010) at a heating rate of 20°C/min from 0 to 250°C under a nitrogen environment. The particle size distributions of latex were carefully observed with transmission electron microscope (Joel, JSM-1200) to elucidate the detail mechanisms.

After a subsequent saponification of latex mixture, PVAc being converted to PVOH, the reaction product was subjected to the similar characterizations, including FTIR and DSC. In addition, a cast film containing starch-g-PVOH and PVOH ($\sim 0.1\text{g}$) was treated with 20 mL of pH7 phosphate buffer solution containing 5 mg of α -amylase for further analysis on the enzymatic biodegradation at 27°C . The degree of weight loss with time was then recorded as an index of biodegradability. Furthermore, the cell culture of fibroblast was carried out in a cell culture medium prepared from a DMEM cell culture solution containing a 10% of FBS and 1% of antibiotics. The film was sterilized first with 70% of alcohol for 30 min and fixed in a 24-well culture plate. The numbers of live cells based on the observation of light spot illuminated from the contact of $10\ \mu\text{L}$ of trypan blue with fibroblast cell solution were determined. Roughly 1 mL of cell solution containing 50,000 of fibroblast cells was transferred to each well. The covered culture well was then incubated in an incubator containing 5% CO_2 at 37°C for 48 h. 1 mL of 10% formaldehyde was employed to immobilize cells on the sample film, followed by an alcohol extraction. The sample dried under a critical point condition for supercritical liquid CO_2 was then sputtered with

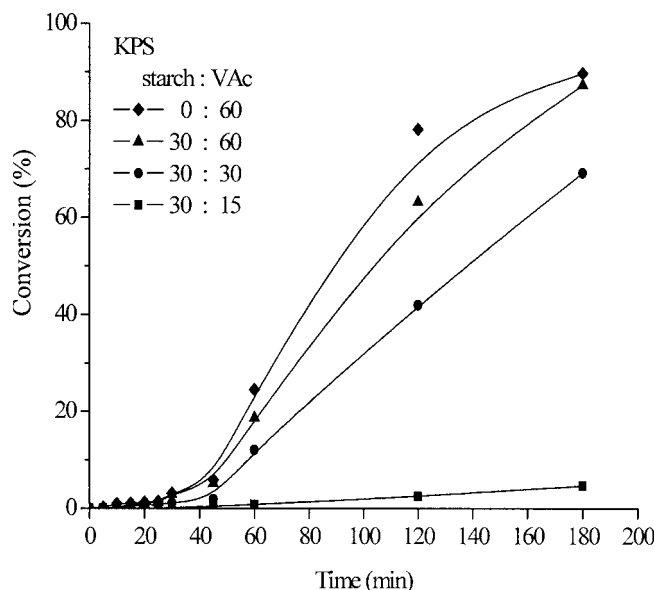


Figure 1 Plots of conversion against reaction time for KPS-initiated systems at various feeding ratios of corn starch to vinyl acetate (reaction temperature, 50°C).

gold and observed in a scanning electron microscope (Joel, JSM-6300) to evaluate the cell growth.

RESULTS AND DISCUSSION

Conversion, grafting ratio, and grafting efficiency

The conversion against reaction time at 50°C for KPS- and CAN-initiated systems at various feeding ratios of corn starch to VAc are shown in Figures 1 and 2, respectively. Basically, conversion steadily increases with the dosages of VAc monomer for both systems. However, differences between two systems were observed. First, in the case of polymerization of pure VAc (in the absence of starch), the level of conversion attained was up to 90% for KPS-initiated system, but only about 35% for CAN case. In particular, for the KPS-initiated VAc polymerization, the mixture observed throughout the course of reaction was milky white and did not show severe coagulation phenomenon as seen for CAN case. This was attributed to the inherent differences in the role of latex stabilization. Initiated persulfate ions with negative charges ($-\text{SO}_4^-$) on the growing PVAc chains tend to stabilize latex particles through electrostatic repulsion mechanism, where the zeta potential was found at -36.3 mV . On the other hand, the initiation from CAN did not provide this stabilization feature.

When the comparison was made on the starch graft copolymerization of VAc, the aforementioned coagulation phenomenon in CAN-initiated system was not observed, suggesting pregelatinized starch seems to serve as a surfactant in stabilizing latex particle. Moreover, the zeta potential of final latex

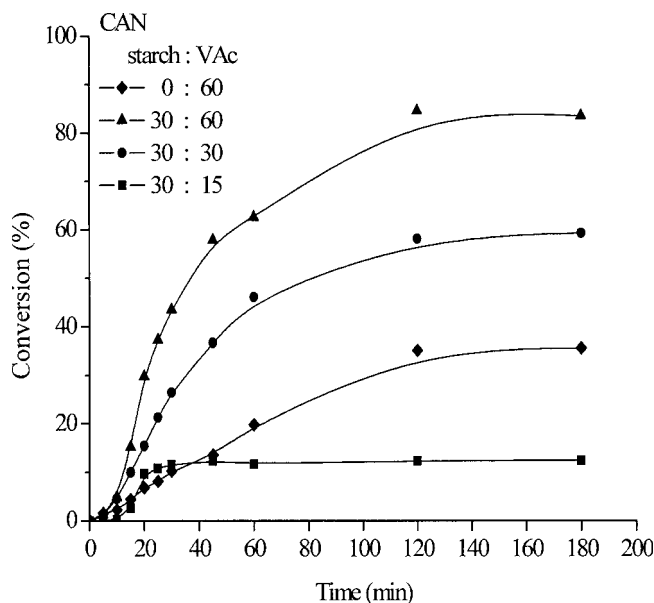


Figure 2 Plots of conversion against reaction time for CAN-initiated systems at various feeding ratios of corn starch to vinyl acetate (reaction temperature: 50°C).

particles for the system with the feeding ratio 30 : 60 (starch to VAc monomer) was found to be 21.5 mV. The conversion was also found to be increased with the amount of VAc monomer added and could reach 84% in the system with a weight ratio of 30 : 60 (starch to VAc monomer) (Fig. 2). In the literature, CAN initiator has been widely used in graft polymerization of synthetic polymer chain onto polysaccharide, where initiation occurs through redox reaction of ceric ion (Ce^{4+}) with pyranose ring. Once free radicals are generated on the pyranose rings, grafted PVAc chains are produced rapidly through propagation of VAc monomer. The produced copolymer thus exhibits hydrophilic starch main chain grafted with hydrophobic PVAc chain. It has been confirmed^{11–13} in a graft polymerization of MMA and VAc monomer onto chitosan, respectively, that a stable emulsion system was observed and the surface of latex particles was in rich of hydrophilic chitosan. A con-

TABLE I
Conversion, Grafting Efficiency and Grafting Ratio under 3 h of Reaction at 50°C for Corn Starch and Vinyl Acetate Having Different Compositions

Starch : VAc	Conversion (%)	Grafting efficiency (%)	Grafting ratio
CAN-initiated system			
30 : 15	12.4	0.6	0.00
30 : 30	59.3	12.1	0.07
30 : 60	83.7	21.5	0.36
KPS-initiated system			
30 : 15	4.7	0.0	0.00
30 : 30	69.2	0.1	0.00
30 : 60	87.3	5.3	0.09

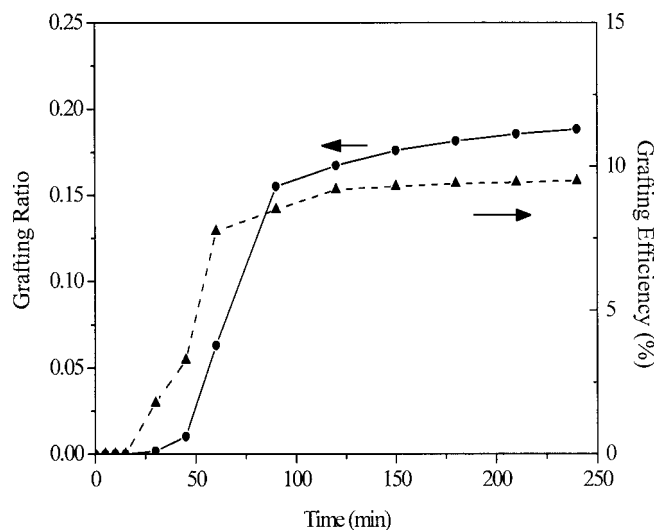


Figure 3 Effect of reaction time on the grafting ratio and grafting efficiency for KPS initiation at 60°C (starch : VAc = 30 : 60, weight ratio).

clusion was therefore made that the produced amphiphilic copolymer could serve as a surfactant.

Moreover, Figure 1 illustrates an induction period contributed to a relatively slow reaction rate for KPS initiation at this reaction temperature, 50°C. Yet, the final values of conversion under 3 h of reaction were slightly larger than those of CAN initiation, as shown in Table I. As for the grafting ratio and grafting efficiency, KPS-initiated system gave a relatively low value indicating a great tendency for the formation of PVAc homopolymer. Yet, higher grafting ratio and grafting efficiency were seen for the CAN-

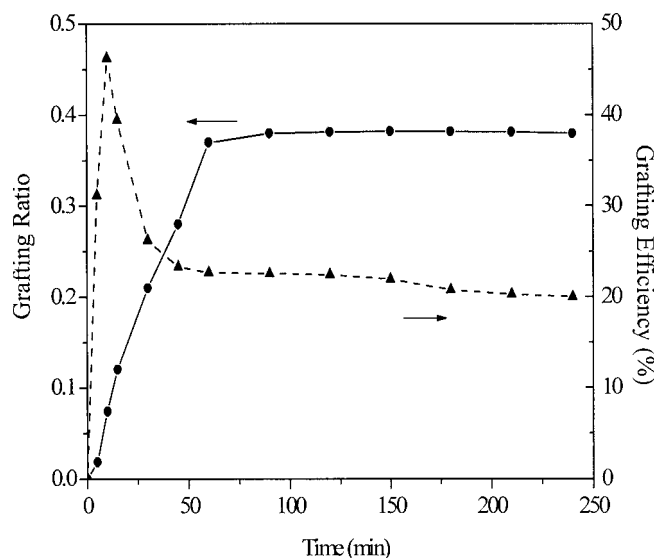


Figure 4 Effect of reaction time on the grafting ratio and grafting efficiency for CAN initiation at 50°C (starch : VAc = 30 : 60, weight ratio).

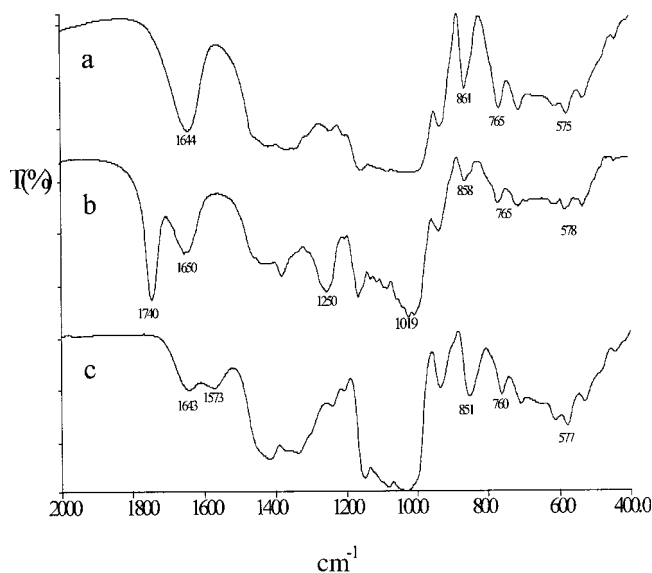


Figure 5 FTIR spectra of (a) corn starch, (b) acetone purified starch-g-PVAc, and (c) starch-g-PVOH for a typical KPS-initiated system.

initiated system, which could reach 0.36 and 21.5%, respectively, for the system with starch: VAc = 30 : 60.

In an effort to further promote the grafting capability in KPS-initiated system, higher reaction temperature was carried out to contrast the effect of various conditions. Figures 3 and 4 indicate the effect of reaction time on the grafting ratio and grafting efficiency for KPS- and CAN-initiated system (starch : VAc = 30 : 60 in weight ratio) at 60 and 50°C, respectively. In the KPS-initiated system, persulfate radicals from thermal dissociation of KPS reacted with VAc monomer to initiate formation of PVAc homopolymer. Therefore, at initial stage of reaction, the reaction was almost dominated by homopolymerization, where grafting efficiency was almost negligible at first half hour of reaction. However, as polymerization proceeded, chain transfer of

radicals from growing polymer to starch occurred and thus initiated graft polymerization of VAc onto starch, similar to the studies in the graft polymerization of methyl methacrylate onto chitosan using KPS initiator.^{11,12} Eventually, a notable increase of grafting ratio and grafting efficiency at correspondent values of 0.18 and 9.5% in comparison to previous measures of very low grafting capability in the reaction system at 50°C was observed. Contrary to a steady increase for KPS initiation, a distinct peak was observed for the CAN-initiated system in the very beginning of reaction giving a comparably high grafting efficiency. This was due to the generation of radicals on starch molecules directly through the redox initiation by CAN for subsequent graft polymerization. As reaction proceeded, grafted PVAc with hydrophobic nature tended to embed inside of pregelatinized starch having hydrophilic nature, forming stable latex particles. During reaction, chain transfer to VAc monomer occurred due to a high chain transfer constant in the VAc polymerization system, a value of $1.75\text{--}2.8 \times 10^{-4}$.¹⁴ This resulted in an increasing homopolymerization rate of PVAc as reaction proceeded. Consequently, these two reactions competed with each other, and after a certain time, grafting probability was greatly reduced. Note that the order of magnitude of grafting ratio and efficiency are in agreement with some published literatures for a similar system,^{7,10} yet a detail mechanism accounts for some subtle difference remains unclear and requires a further study.

Spectroscopic, molecular weight, and thermal characterization

The FTIR spectra of unmodified corn starch, acetone purified starch-g-PVAc, and starch-g-PVOH are depicted in Figure 5 for a typical KPS-initiated system. Figure 5(a) shows the characteristic absorption bands

TABLE II
Number Average Molecular Weight (M_n), Weight Average Molecular Weight (M_w), and Their Ratio (M_w/M_n) of PVAc Homopolymer and Grafted PVAc for Two Different Initiated Systems

Feeding composition (Starch : VAc)	Homopolymer PVAc ^a			Grafted PVAc ^b		
	$M_w (\times 10^4)$	$M_n (\times 10^4)$	M_w/M_n	$M_w (\times 10^4)$	$M_n (\times 10^4)$	M_w/M_n
CAN-initiated system						
30 : 15	NA	NA	NA	NA	NA	NA
30 : 30	5.20	1.93	2.69	5.61	1.77	3.17
30 : 60	11.25	3.00	3.75	23.60	7.51	3.14
KPS-initiated system						
30 : 15	NA	NA	NA	NA	NA	NA
30 : 30	17.74	4.75	3.73	NA	NA	NA
30 : 60	45.48	11.42	3.98	55.00	16.05	3.42

Number average-, weight average-molecular weight and their ratio of pure PVAc synthesized by free radical polymerization using KPS initiator were 80.66×10^4 , 28.06×10^4 , and 2.88, respectively.

^a Homopolymer was obtained by acetone extraction.

^b Grafted PVAc was obtained by HCl degradation of starch-g-PVAc copolymer.

TABLE III
Glass Transition Temperatures (T_g) and Melt
Temperatures (T_m) of Graft Copolymers for Two
Different Initiated Systems

Starch : VAc	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
CAN-initiated system		
30 : 15	–	–
30 : 30	44	220
30 : 60	40	222
KPS-initiated system		
30 : 15	–	–
30 : 30	–	237
30 : 60	37	242

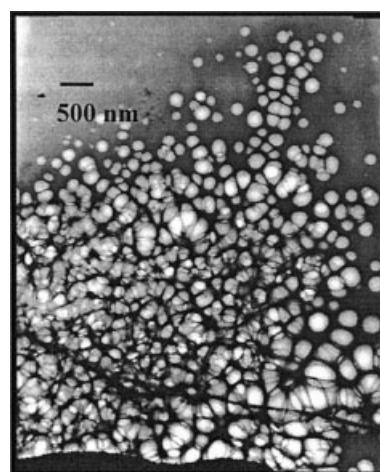
T_g of pure PVAc was at 37°C ; endothermic peaks of corn starch were observed at 150 ; 227°C . “–”, transition or peak is not discernible.

of starch at 575 , 765 , and 861 cm^{-1} . Additional specific peaks at 1250 , and 1740 cm^{-1} corresponding to $(\text{O}-\text{C})=\text{O}$ and $\text{O}-(\text{C}=\text{O})$ stretching vibration in ester group, respectively, in Figure 5(b) confirm the existence of grafted poly(vinyl acetate). Further saponification of grafted PVAc to PVOH is clearly indicated in Figure 5(c) with a disappearance of absorption bands from ester group. Similar conclusions are also reached for the CAN-initiated system.

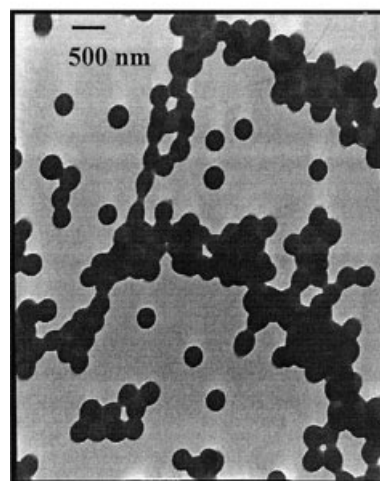
Table II lists the number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity (PD) of PVAc homopolymer and grafted PVAc for both KPS- and CAN-initiated systems at various compositions under reaction temperature at 50°C . Note that some values indicated as NA are due to an encountered difficulty in harvesting small amounts of reaction products. Grafted PVAc chains were obtained through a hydrochloric acid treatment on starch copolymer. In general, regardless of the different feeding ratio of starch and VAc in this study, molecular weights of extracted PVAc homopolymer and grafted PVAc for KPS-initiated system were significantly higher than those for CAN initiation, respectively, up to four times difference. Two explanations are considered for the shorter chain length observed for CAN-initiated system. First, production rate of free radicals through redox reaction as in CAN case is general higher than that from thermal dissociation of initiator like KPS. Therefore, initiation rate was higher for CAN-initiated system especially at the early stage of reaction, as can be seen when Figures 1 and 2 were compared. Therefore, polymer chain length would be shorter due to higher concentration of growing polymer radicals. Secondly, it is known in the literature¹⁵ that the ceric ion (Ce^{4+}) also could terminate the propagating chains, $\text{PVAc}\cdot + \text{Ce}^{4+} \rightarrow \text{PVAc} + \text{Ce}^{3+} + \text{H}^+$, thus decreasing PVAc chain length.

Glass transition temperatures (T_g) and melt temperatures (T_m) recorded from differential scanning

calorimeter are indicated in Table III for two different initiated systems. Apparently, glass transition temperature of PVAc increased slightly due to a possible constraint stemming from inherently rigid structure of native starch for both KPS- and CAN-initiated systems. No notable difference was found on the effect of initiators on the glass transition temperature. As for melt temperatures, corn starch originally exhibits two endothermic peaks at 150 and 227°C , which then vary differently but not much depending on grafted systems. As saponification was carried out to convert PVAc to PVOH, DSC thermograms were also recorded on starch-g-PVOH. Glass transition and melting temperature of pure PVOH were observed at 79 and 229°C , respectively. The glass transition temperature of PVOH increased to 81°C and 82°C for KPS- and CAN-initiated system, respectively.



(a)



(b)

Figure 6 TEM micrographs of (a) $\times 40,000$ gelatinized corn starch, and (b) $\times 12,000$ pure PVAc synthesized by free radical polymerization using KPS as initiator after 3 h of reaction.

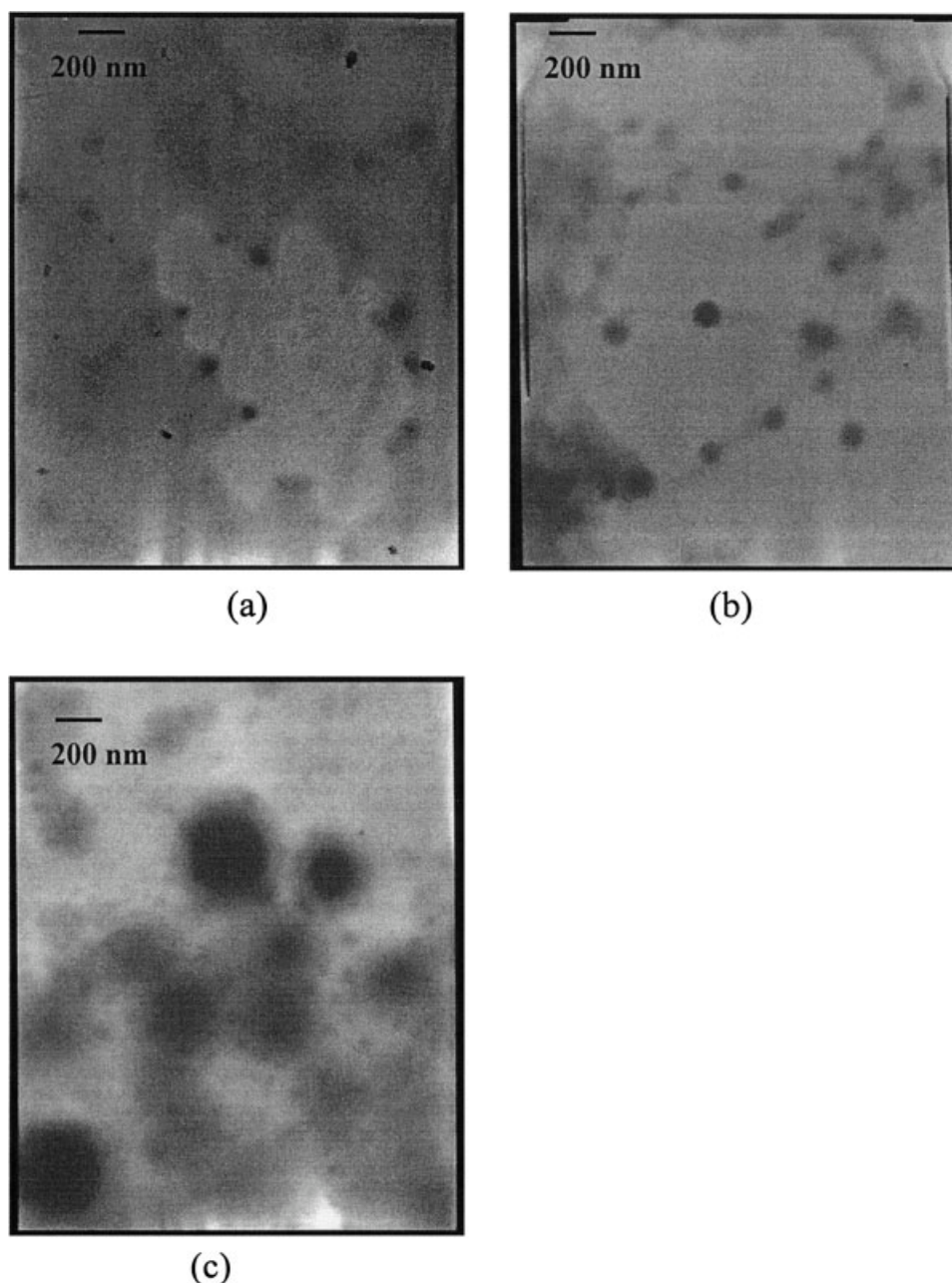


Figure 7 TEM micrographs ($\times 40,000$) of KPS-initiated graft reaction for 3 h at various compositions of starch : VAc = (a) 30 : 15, (b) 30 : 30, (c) 30 : 60.

Moreover, it is interesting to find that distinct melting peaks from starch and PVOH remain distinguishable for KPS-initiated system, but tend to merge as a broad band for the CAN case, especially for a composition of starch : VAc = 30 : 60. It implies the interaction between starch and grafted PVOH is not strong enough to affect the individual crystallization behavior for the former case. This might be ascribed to the longer chain length of grafted PVOH (suggested from the data in Table II) and smaller grafting ratio (Table I) in KPS-initiated system. Consequently, phase morphology would also be affected, which is discussed in the following section.

Morphological observations

Figure 6 shows the TEM micrographs of gelatinized corn starch (a) and pure PVAc using KPS as initiator after 3 h of polymerization reaction (b), respectively. As no extra surfactant added in the polymerization of pure PVAc, persulfate radicals with negative charge might serve as surfactant to stabilize growing polymer particles through electrostatic repulsion effect. After 3 h of reaction, a uniform particle size distribution of PVAc particles with ~ 300 nm in diameter was observed.

When corn starch was added and graft reaction was carried out for the same duration of 3 h in KPS-initiated system, the final particle size distribution

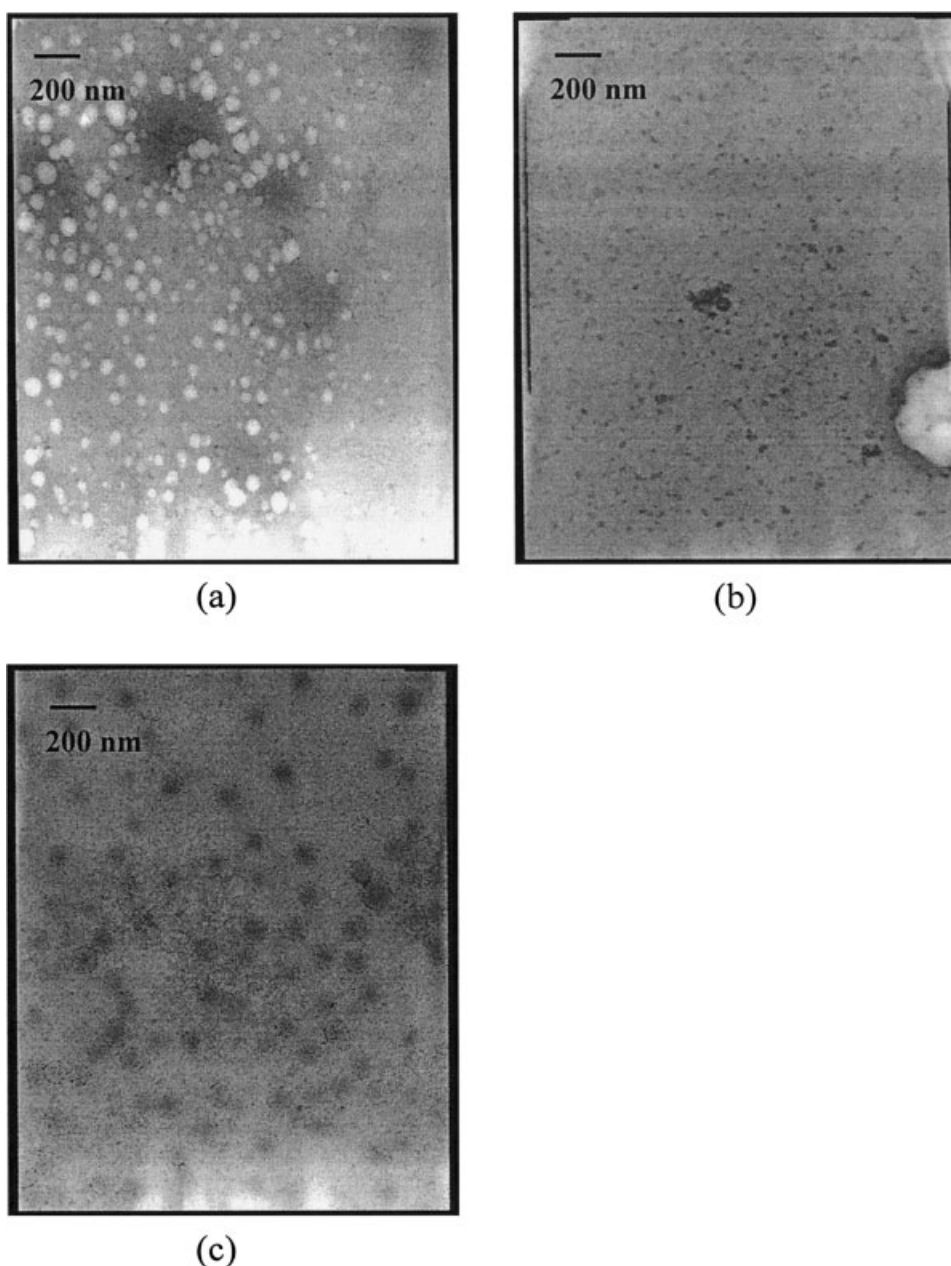


Figure 8 TEM micrographs ($\times 40,000$) of CAN-initiated graft reaction for 3 h at various compositions of starch : VAc = (a) 30 : 15, (b) 30 : 30, (c) 30 : 60.

became broad for all the compositions investigated, shown in Figure 7. As the concentration of VAc monomer increased, particle size increased and aggregations were even more severe. Apparently, original stabilizing factor through electrostatic repulsion for the homopolymerization of PVAc was suppressed. The zeta potential of latex particles decreased greatly from original -36.3 mV for pure PVAc latex particles to a value of only -3.5 mV for the system with starch : VAc = 30 : 60. It was suggested that the hydrophobic nature of PVAc would tend to migrate into the core of particle. Accordingly, surface charge density of particles appeared to be not

sufficient to maintain stability, especially at later stage of reaction.

On the other hand, a uniform particle size distribution was found for graft copolymerization using CAN as initiator, shown in Figure 8. As we mentioned earlier, starch macroradicals were formed through a direct redox reaction between CAN and pyranose ring for a CAN initiation system. The hydrophobic PVAc chains thus were grafted on hydrophilic starch, resulting in an amphiphilic graft copolymer where PVAc chains were embedded inside the latex particles. Furthermore, it was found that the zeta potential of gelatinized starch after addition of

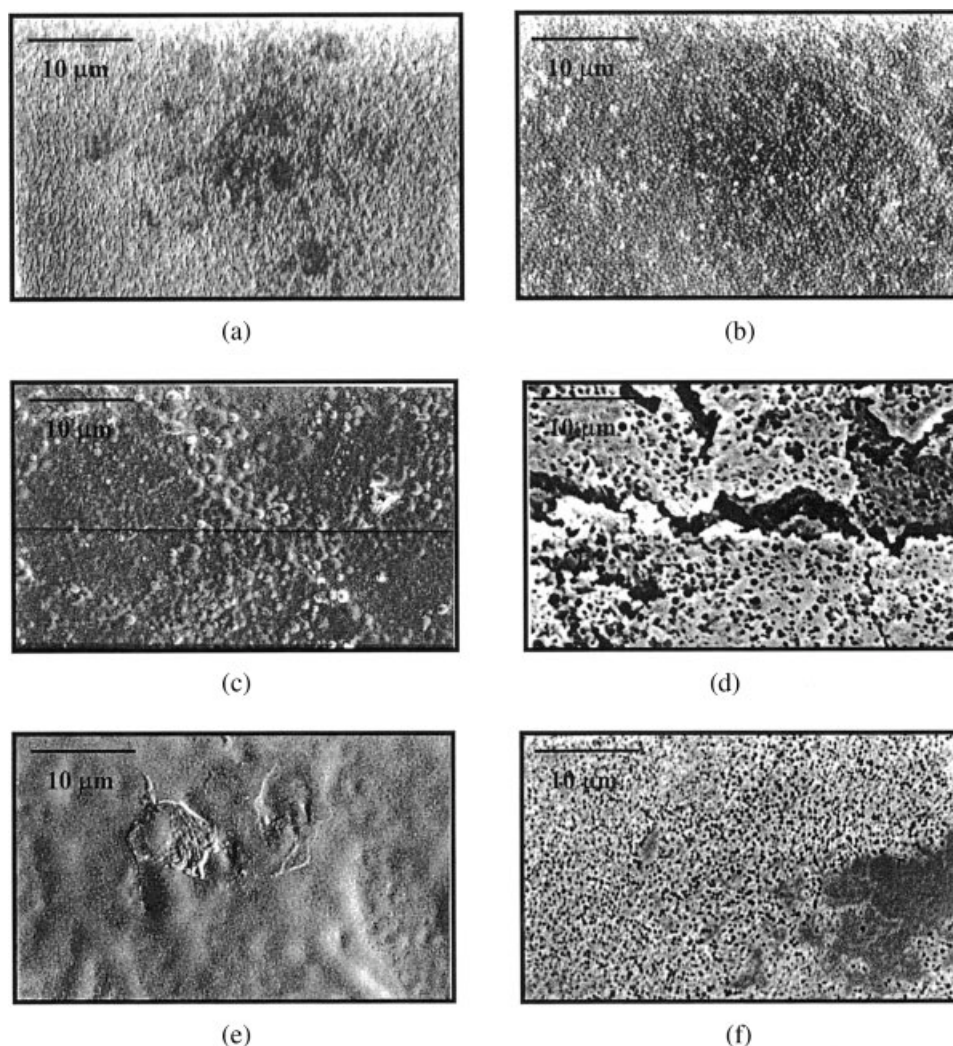


Figure 9 SEM micrographs ($\times 3000$) of surface texture for (a) starch (b) pure PVAc by KPS initiation (c) reaction product of a KPS-initiated system with starch : VAc = 30 : 60 (d) acetone treated reaction product of a KPS-initiated system with starch : VAc = 30 : 60 (e) reaction product of a CAN-initiated system with starch : VAc = 30 : 60 (f) acetone treated reaction product of a CAN-initiated system with starch : VAc = 30 : 60.

CAN was 17.5 mV. After polymerization by the subsequent addition of VAc monomer, the zeta potential became more positive, 21.5 mV. Thus, hydrophilic and positive-charged starch mostly on the surface of particles seemed to provide a sufficient stabilization degree as a role of surfactant to render a relatively uniform distribution of latex particles. For example, the particle size was about 100 nm for the system with a starch : VAc composition of 30 : 60 in weight ratio.

To further elucidate the differences in grafting mechanism for these two initiated systems, scanning electron microscope was used to observe the distinct morphology of surface texture of a representative composition of starch : VAc acetate = 30 : 60 (Figure 9). No much difference on the surface was observed. On the other hand, after samples were treated with acetone to extract PVAc homopolymer, relatively smaller cavities in an even distribution were seen for

CAN-initiated system [Fig. 9(f)] rather than the KPS case [Fig. 9(d)]. If one recalls the previous discussions on DSC measurements, two distinct melting peaks from starch and grafted PVOH remain distinguishable for KPS-initiated system, but tend to merge as a broad band for CAN case. These independent findings support a stronger interaction between starch and PVOH chains for a CAN initiated graft reaction. Most interesting, latex particles are generally uniform for CAN initiation through TEM observations discussed in the previous section.

Biodegradability and cell culture capability

The latex solution after 3 h of reaction was subjected to saponification to convert PVAc to PVOH. The prepared starch-g-PVOH/PVOH film was then treated

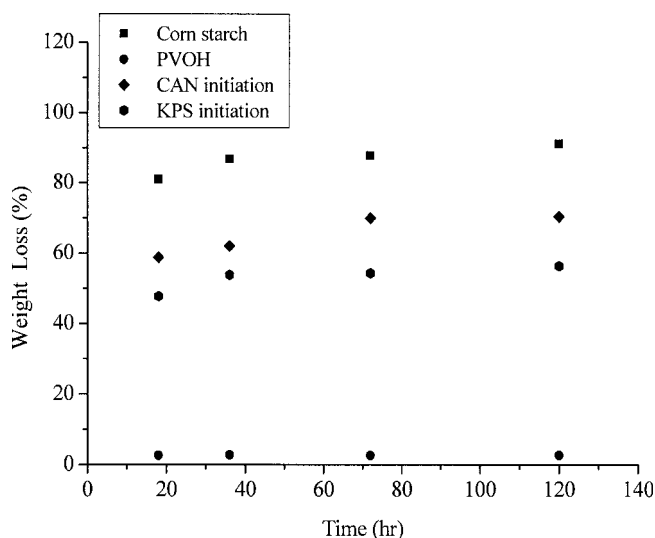


Figure 10 Degree of weight loss as an index of biodegradability through enzymatic hydrolysis for a representative composition of starch : VAc = 30 : 60 initiated with two different systems.

with α -amylase for further analysis on the enzymatic biodegradation. Figure 10 shows the degree of weight loss as an index of biodegradability through enzymatic hydrolysis for a representative composition of starch : VAc = 30 : 60 in two different initiated systems. Starch and pure PVOH were also evaluated as a control for comparison. It is known α -amylase would convert α -1,4 glycoside bonds on starch into dextrin, glucose, etc, which then dissolved into water subsequently. The total weight loss for pure starch over 120 h reached up to 90%. On the other hand, relatively low level of weight loss was seen

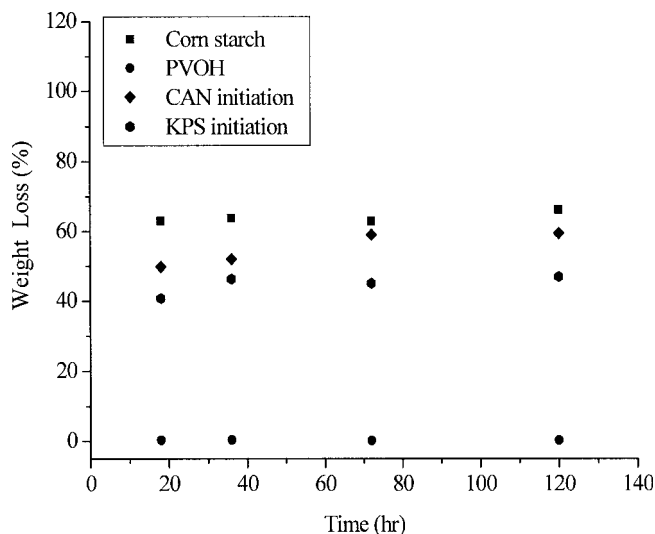
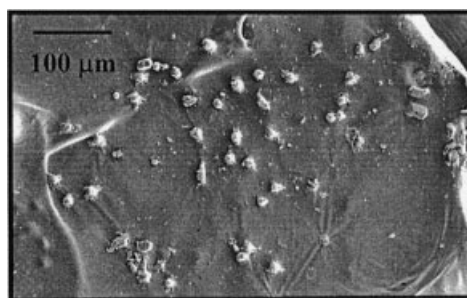
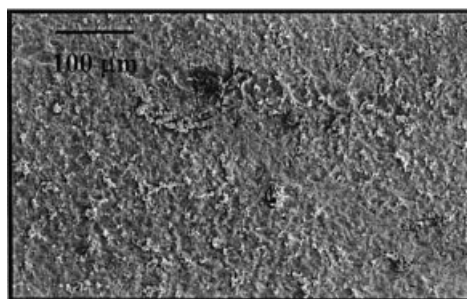


Figure 11 Degree of weight loss as an index of biodegradability through enzymatic effect only for a representative composition of starch : VAc = 30 : 60 initiated with two different systems.

for PVOH (3%) in light of the unique selectivity of enzyme effect. As for graft copolymer, the weight loss attained was about 70 and 56% for CAN- and KPS-initiated system, respectively. In addition, a slightly higher weight loss was also observed for other investigated compositions initiated by CAN. If one assumed a simple mixing rule for the weight loss by enzymatic degradation, i.e., the weight loss was contributed independently by each component (90% for starch and only 3% for pure PVOH), the theoretical values of weight loss thus can be calculated with the help of conversion data in Table I. They were 49.9% and 48.9% for CAN- and KPS-initiated system, respectively. Apparently, the observed weight loss was higher than the calculated value for both systems. It was then suspected that the dissolved starch oligomers produced by enzymatic deg-



(a)



(b)



(c)

Figure 12 SEM micrographs ($\times 200$) of cell culture of fibroblast for KPS-initiated starch-g-PVOH films at various compositions of corn starch : VAc = (a) 30 : 15 (b) 30 : 30 (c) 30 : 60.

radation were accompanied with most of the grafted PVOH chains bonded on starch chains, thus resulting in higher weight loss. If the weight of grafted PVOH (derived from Table I) was accounted for the weight loss, the calculated values became 58.5% and 51.4%, which were close to the experimental values. The higher value observed in CAN-initiated system is explained by its higher grafting ratio and lower chain length of PVOH. To further confirm this, the weight loss directly from hydrolysis without adding enzyme was measured under the same conditions. This value was then subtracted from the weight loss due to enzymatic degradation to exclude the effect of water hydrolysis and solubility. A similar conclusion was reached, as shown in Figure 11.

The cell culture of fibroblast was carried out as an indication for the cell compatibility, shown in Figure 12. Only starch-g-PVOH/PVOH films from KPS-initiated systems are presented here since the cell growth was not observed clearly in the cases of starch, PVOH, and starch-g-PVOH/PVOH under CAN-initiated system. For a composition of starch : VAc = 30 : 15, particulate cells distributed irregularly, shown in Figure 12(a). In the case of equal composition of starch and VAc, Figure 12(b), only cell attachment was observed. On the other hand, the growth of filopodia, cytoplasmic webbing, and flattening behavior, see Figure 12(c), were observed for a composition of starch : VAc = 30 : 60, indicating a very good culture capability.¹⁶ Owing to several factors affecting the cell growth capability, including surface texture, crystallinity, etc., it is hard to account for this observed difference simply based on the feeding composition.

CONCLUSIONS

The vital differences in the structural characteristics and properties for resulting polymers from the starch/VAc systems initiated with KPS and CAN, respectively, are thoroughly discussed in this study. In the KPS-initiated system, anionic persulfate radicals ($-\text{SO}_4^-$) from thermal dissociation of KPS reacted with VAc monomer to initiate formation of PVAc homopolymer. Therefore, the reaction was almost dominated by homopolymerization. As polymerization proceeded, chain transfer of radicals from growing polymer to starch occurred and thus initiated graft polymerization of VAc monomer onto starch. However, this chain transfer reaction was very slow and observable grafting ratio was only obtained at higher reaction temperatures. Moreover, there was a decrease in surface charge density of latex particles when the polymerization was carried out in the presence of starch. Accordingly, surface charge density of particles appeared to be not sufficient to maintain stability. Contrary to the KPS initiation, radicals were directly generated on starch molecules

through a redox reaction between ceric ion and pyranose ring for a CAN initiation system. As a result, higher grafting ratio and grafting efficiency were seen for the CAN-initiated system under the same reaction conditions. The hydrophobic PVAc chains thus were grafted on hydrophilic starch, resulting in an amphiphilic graft copolymer where PVAc chains were embedded inside the latex particles. Thus, hydrophilic and positive-charged starch seemed to provide a sufficient stabilization degree as a role of surfactant to render a relatively uniform distribution of latex particles. During reaction, chain transfer to VAc monomer occurred due to a high chain transfer constant in VAc polymerization system, leading to homopolymerization of PVAc. Consequently, these two reactions competed with each other. The ceric ion also could terminate the growing polymer chains by chain transfer reaction, leading to shorter chain length in CAN-initiated system. When the PVAc chains were converted to PVOH chains by saponification, a stronger interaction between grafted PVOH chains and starch molecules was observed for CAN-initiated system because of the higher grafting ratio and lower grafted chain length. This also resulted in a higher weight loss in enzymatic degradation.

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