Emulsion Grafting of Vinyl Acetate onto Preirradiated Poly(3-hydroxybutyrate) Film

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ABSTRACT: Vinyl acetate (VAc) was grafted onto poly(3-hydroxybutyrate) film by a preirradiation method. Grafting reactions were carried out in VAc/water/surfactant emulsion, VAc/water, and VAc/methanol systems. For emulsion grafting, Nonion L-4 was ascertained to be the optimum surfactant with respect to the stability of a single emulsion layer. The emulsion with a 10 : 1 (w/w) ratio of VAc to surfactant yielded the highest degree of grafting: 23%. The grafting efficiency in the emulsion and the water and methanol solvents were evaluated. The results indicated that the grafting efficiency of the emulsion was 100 times that of VAc/methanol when the same 2 wt % VAc was used in the grafting reaction. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2289–2294, 2008

Key words: graft copolymers; particle size distribution; solution properties

INTRODUCTION

The control of the biodegradability of biodegradable polymers such as poly(3-hydroxybutyrate) (PHB) and its copolymers is the most important aspect that needs to be addressed for practical applications.[1–4] For practical usage, favorable performance of biodegradable polymers means preserving their mechanical strength and enabling their degradation immediately after use.

To realize this, many approaches have been adopted. One of the methods is to control the biodegradability by means of surface modification of biodegradable polymers by grafting. In previous studies, we attempted to graft various monomers onto a PHB film to control its biodegradability.[5–9] The enzymatic degradability of a PHB film grafted with acrylic acid (AAc) was drastically suppressed with an increase in the degree of grafting (X_g) because nondegradable AAc covered the surface of the PHB film.[10] After the thermal remolding of PHB-*g*-AAc films, biodegradable PHB appeared on the surface. Furthermore, the biodegradability of PHB-*g*-AAc was retained. Thus, the combination of AAc grafting and thermal remolding is useful in achieving the control of the biodegradability of biodegradable polymers.[11] However, this method has a disadvantage: the AAc graft chains do not degrade after the enzymatic degradation of AAc-grafted PHB.

Then, it was necessary to graft the monomer onto PHB film that could be degraded completely after biodegradation. In this study, we attempted to graft vinyl acetate (VAc) onto a PHB film because the grafted poly(vinyl acetate) could be transformed into degradable poly(vinyl alcohol) (PVA) after saponification treatment. It is known that PVA can be degraded completely by a degradative enzyme.[12,13] Thus, the purpose of grafting VAc onto the PHB film is to obtain a film with controllable biodegradability and the ability to degrade completely after saponification.

The PHB grafted with VAc films (PHB-*g*-VAc) was prepared by preirradiation techniques of radiation-induced graft polymerization. X_g was controlled by changes in the monomer concentration during a typical grafting reaction. However, the polymerization reactivity of the VAc monomer was very low. Therefore, some VAc polymerization methods were studied to improve the polymerization reactivity. As one of the improved processes, VAc emulsion polymerization has been extensively studied.[14] The degree of polymerization of VAc was increased exponentially by the use of this emulsion polymerization method. In this study, we applied this emulsion polymerization method to the grafting reaction of VAc on the surface of PHB films. Initially, the best surfactant was selected on the basis of the stability of the VAc emulsion prepared. We then investigated the optimum VAc and surfactant concentrations during the grafting reaction. The grafting reactivity of the emul-

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sion system was compared with those of VAc/water, VAc monomer, and VAc/methanol systems.

EXPERIMENTAL

Materials

Microbial PHB, purchased from Sigma-Aldrich Chemical Co., Ltd. (St. Louis, MO), was purified as follows to remove the protein and impurities: the PHB was dissolved in chloroform and then poured into a solvent mixture comprising *n*-hexane and methanol (1 : 1 vol %). The precipitated PHB was filtered and dried in a vacuum. The purified PHB powder was preheated at 190°C for 3 min and hot-pressed at 150 kgf/cm^2 at the same temperature for 5 min. Then, the obtained films, 150 μm thick, were cooled with a cold press for 5 min. The PHB films were crystallized isothermally at 90°C for a week before use. The VAc was purchased from Kanto Chemical, Inc., and used without further purification.

Preparation of the grafted PHB film with VAc

Emulsification of VAc in water

VAc emulsion solutions with various surfactants (VAc/surfactant/water = 10 : 1 : 89 wt %) were stirred with a stirrer for 5 min at room temperature, and their stability was observed at intervals of 3 h. The following surfactants were used: sodium *n*-dodecyl sulfate (anion; Kanto), Amphitol 86B (stearyl betaine, cation; Kao Co., Ltd.), Latemul E-150 (polyoxyethylene, cation; Kao), Cation BB (cation; Nof Co., Ltd.), Quartamin (ammonium chloride, cation; Kao), Emulgen 120 (polyoxyethylene and lauryl ether, nonion; Kao), Nonion NS-206 (polyether, nonion; Nof), Elec TS-2B (polyoxyalkylene, nonion; Kao), Rheodol TW-L120 (polyoxyethylene, nonion; Kao), Tween 20 [polyethylene (20) sorbitan monolaurate, nonion], Tween 80 [polyethylene (20) sorbitan monolaurate, nonion; Kanto], and Nonion L-4 (polyether, nonion; Nof Co). Then, the emulsion solutions, which formed a single layer, were heated up to 60°C in a water bath to select the most suitable surfactant at the grafting temperature.

Radiation graft polymerization of VAc onto the PHB films

The PHB films were cut into pieces of 10 mm × 60 mm (ca. 12 mg); six of these pieces were packed into polyethylene bags. After the air in the bags was substituted with nitrogen, the PHB films were irradiated with electron beams (Cockcroft-Walton type) at a voltage and current of 2 MeV and 3 mA, respectively. The total doses were changed to the range of 10–100 kGy. These irradiated PHB films were placed in a glass reactor, and the air in the reactor was removed. Then, these films were placed in contact with 150 mL of a deaerated VAc emulsion solution (1–15 wt % VAc and 10 : 1 w/w VAc/surfactant). This was done in the same manner with other VAc systems in which methanol and water were used as solvents. The reaction temperature was maintained at 60°C by the dipping of the glass reactors in a warm water bath. After the grafting reaction, the grafted PHB films were immersed in methanol for an hour at 60°C to remove the VAc monomer and homopolymer. In this grafting reaction, X_g was calculated with the following equation:[15]

$$X_g\,(\%) = (W_g - W_0) \times 100/W_0$$

where W_0 and W_g are the weights of the PHB films before and after the graft polymerization, respectively.

Measurement of the micelle size distribution of the emulsion

The average micelle diameters of the VAc emulsions were determined by dynamic light scattering (FPAR-1000 particle size analyzer, Otsuka Electronics Co., Ltd., Japan) after 5 min of homogenization at 60°C. The diffusion coefficient was calculated with the Einstein–Stokes expression with an approximate quantity obtained from the cumulant method.[16] The measuring time was fixed at 180 s, and which dust cut was carried out in the range of the upper 10% and lower 100% before measurement.

RESULTS AND DISCUSSION

Grafting of VAc onto the PHB film by emulsion

Emulsion stability

Initially, the VAc emulsion was prepared by the mixing of various surfactants with VAc in water to find the most stable VAc emulsion. In a previous study, Ohmura et al.[17] investigated the effect of aggregation on the micelle size distribution during the continuous emulsion polymerization of VAc. They reported that a high electrostatic repulsion was required to avoid micelle aggregation. Furthermore, they concluded that a mixture of nonionic (Tween 80) and anionic (sodium *n*-dodecyl sulfate) surfactants was very effective in achieving high electrostatic repulsion. However, phase separation occurred in this emulsion solution at the grafting reaction temperature (60°C). Therefore, new studies were conducted on surfactants that could be used in grafting reactions. Various surfactants were tested to achieve a stable emulsion of VAc.

To confirm the stability of the emulsion, VAc, various surfactants, and water were mixed in the ratio of 10 : 1 : 89 (wt %), respectively. The emulsion stabilities

TABLE I
Emulsion Stabilities of VAc with Various Surfactants

No.	Surfactant	VAc concentration (wt %)	Surfactant (wt %)	Elapsed time			
				3 h	6 h	12 h	6 h at 60°C
1	Sodium dodecyl sulfate	10	1	×	×	×	×
2	Amphitol 86B	10	1	×	×	×	×
3	Latemul E-150	10	1	×	×	×	×
4	Cation BB	10	1	×	×	×	×
5	Quartamin	10	1	○	△	×	×
6	Emulgen 120	10	1	×	×	×	×
7	Nonion NS-206	10	1	△	×	×	×
8	Elec TS-2B	10	1	△	△	×	×
9	Rheodol TW-L120	10	1	○	○	○	×
10	Tween 20	10	1	○	○	○	△
11	Tween 80	10	1	○	○	○	△
12	Nonion L-4	10	1	○	○	○	○
13	Nonion L-4	5	0.5	○	○	○	○

× = phase separation; △ = rough emulsion; ○ = stable emulsion.

of VAc with various surfactants are listed in Table I. In this study, the emulsion stability was evaluated with three types of symbols: phase separation (× in Table I), which implies that VAc and water segregate into two layers; rough emulsion (△ in Table I), which implies that the emulsion solution segregates into two layers gradually; and stable emulsion (○ in Table I), which implies that VAc and water form a single layer. Emulsion solutions prepared with sodium dodecyl sulfate, Amphitol 86B, Latemul E-150, Cation BB, and Emulgen 120 surfactants could not maintain a single emulsion layer after 3 h. Emulsion solutions prepared with Quartamin, Noion NS-206, and Elec TS-2B could not maintain a single emulsion layer after 6 h. However, emulsion solutions prepared with Rheodol TW-L120, Tween 20, Tween 80, and Nonion L-4 surfactants maintained a single emulsion layer after 12 h. Then, these stable emulsion solutions were heated up to 60°C in a water bath to select the most suitable surfactant at the grafting temperature. It was observed that Nonion L-4 could maintain the stability of the VAc emulsion after 6 h at 60°C. Then, the emulsion stability at another VAc concentration (VAc/Nonion L-4/water = 5 : 0.5 : 94.5) was verified. This emulsion solution was also stable after 6 h at 60°C. On the other hand, the emulsion solutions prepared with the Rheodol TW-L120, Tween 20, and Tween 80 surfactants underwent phase separations at 60°C. On the basis of these results, we can conclude that a stable VAc emulsion can be achieved with only the Nonion L-4 surfactant. Therefore, Nonion L-4 was used as the surfactant in the subsequent experiments.

Effect of the concentration of the surfactant and VAc on X_g

The emulsion grafting of VAc was carried out with Nonion L-4 as a surfactant. A stable emulsion was obtained when 0.2–1.0 wt % Nonion L-4 was mixed with 5 wt % VAc. Figure 1 shows the effect of the reaction time on X_g when the surfactant concentrations were 0.3, 0.5, and 0.7 wt % and the VAc concentration was 5 wt %. X_g increased with the reaction time. The maximum X_g (23%) was achieved when the emulsion solution with 5 wt % VAc and 0.5 wt % surfactant was used for a 5-h reaction. When the emulsion solution with 0.3 or 0.7 wt % surfactant was used, X_g decreased in comparison with that obtained when the emulsion solution with 0.5 wt % surfactant was used. Thus, it was hypothesized that X_g depends on the surfactant concentration.

The effect of the Nonion L-4 concentration on X_g was investigated in detail. Figure 2 shows the effect of the Nonion L-4 concentration on X_g for a 1-h reac-

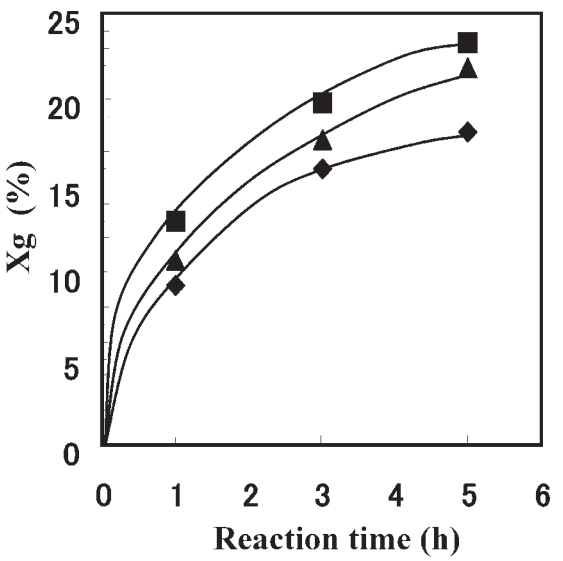

Figure 1 Relationship between the reaction time and X_g: (◆) 0.3, (■) 0.5, and (▲) 0.7 wt % surfactant.

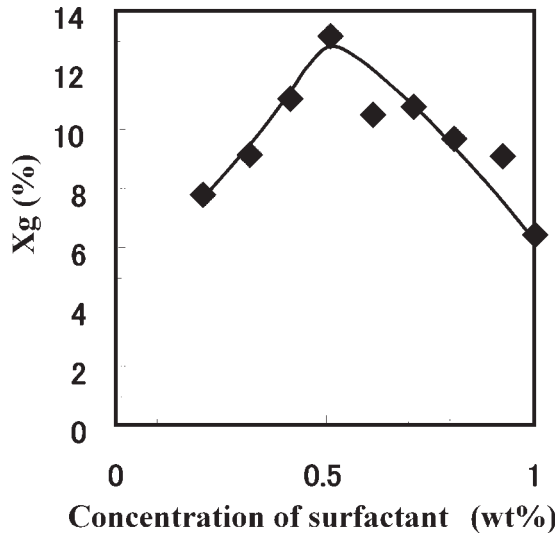

Figure 2 Effect of the concentration of the surfactant on X_g (VAc concentration = 5 wt %).

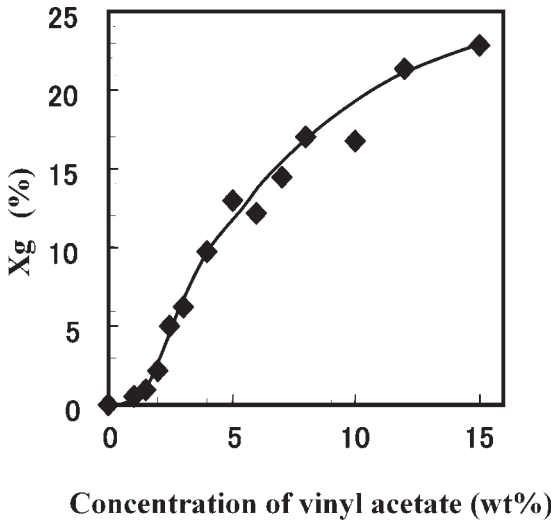

Figure 3 Effect of the VAc concentration on X_g (VAc-to-surfactant ratio = 10 : 1).

tion when the concentration of VAc was 5 wt %. X_g varied with the change in the surfactant concentration regardless of the VAc concentration, which was constant. X_g increased with the surfactant concentration when it was below 0.5 wt %. However, X_g decreased with a further increase in the surfactant concentration. The highest X_g value was 13 wt % when the surfactant concentration was 0.5 wt %.

To investigate the relationship between the micelle size of the VAc and surfactant concentration, the micelle diameters of the emulsion solutions were measured; these values are listed in Table II. The micelle diameter of the VAc decreased with the increase in the surfactant concentration when it was less than 0.5 wt %. However, the micelle size increased with the surfactant concentration when it was more than 0.5 wt %. The diffusion coefficient of micelles increased with the decrease in the micelle size.

There exists a relationship between the micelle size and X_g. The X_g value increases with a decrease in the micelle size. This implies that the surface area of micelles increased as their size decreased. As a result, the probability that the micelles would come in contact with the PHB film increased, and therefore X_g increased (shown in Table II and Fig. 2). On the basis of this result, it was thought that the 10 : 1 (w/w) ratio of the VAc and surfactant was optimum for the emulsion solution. Figure 3 shows the effect of the VAc concentration on X_g when the VAc/surfactant ratio in the emulsion solution was constant—10 : 1 (w/w)—for a 1-h reaction. X_g increased with the monomer concentration. The highest X_g was 23 wt % in the case of 15 wt % VAc for the 1-h reaction. Thus, X_g could be easily controlled to change the monomer concentration in the solution.

TABLE II
Effect of the Surfactant Concentration on the Micelle Diameter and Diffusion Coefficient

Sample no.	VAc monomer concentration (wt %)	Surfactant	Micelle size (nm)	Diffusion coefficient (cm^2/s)
1	5.0	0.2	550	1.80×10^{-6}
2	5.0	0.3	435	2.41×10^{-6}
3	5.0	0.5	380	2.76×10^{-6}
4	5.0	0.7	430	2.46×10^{-6}
5	5.0	1.0	990	1.06×10^{-6}

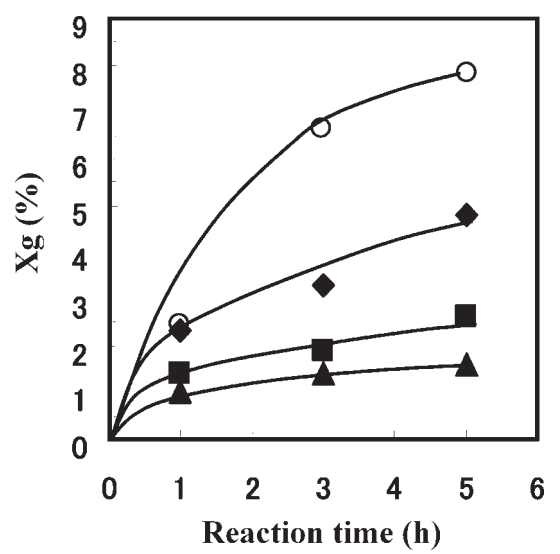

Figure 4 Relationship between the reaction time and X_g when water was used as the solvent: (◆) 2 wt % VAc, (■) 1.5 wt % VAc, (▲) 1 wt % VAc, and (○) 2 wt % VAc emulsion solution.

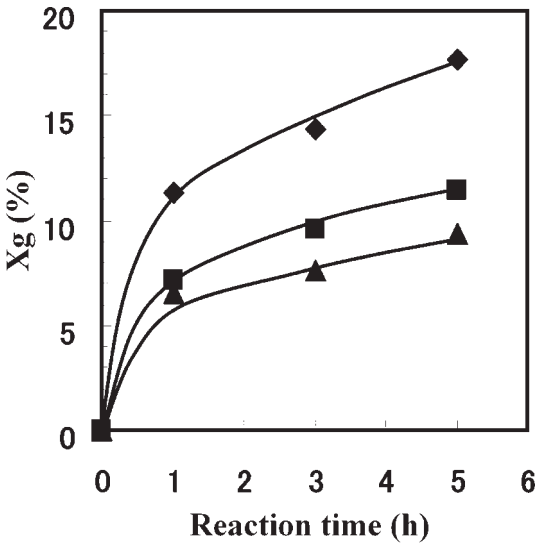

Figure 5 Relationship between the reaction time and X_g when methanol was used as the solvent: (◆) 100, (■) 90, and (▲) 80 wt % VAc.

Grafting of VAc onto the PHB film with VAc/water and VAc/methanol

Grafting of VAc onto the PHB film with VAc/water

VAc emulsion polymerization has been extensively studied since the 1960s and 1970s,[14] and several studies have been conducted on the kinetics of emulsion polymerization of VAc. However, the results of these experimental polymerizations varied widely. Some researchers proposed that a significant amount of polymerization occurs in the aqueous phase. Other researchers suggested that polymerization primarily occurs in the monomer-swollen polymer particles.[18–21] Thus, the graft polymerization of VAc was performed with water as a solvent.

Only 2% of the VAc dissolved in the water. Figure 4 shows the effect of the reaction time on X_g with VAc/water solutions. X_g increased with the reaction time for each concentration value. The maximum X_g was 5% in the 2 wt % VAc aqueous solution for a 5-h reaction.

Figure 4 shows the effect of the reaction time on X_g in a 2 wt % VAc emulsion solution with a constant VAc/surfactant ratio of 10 : 1. The value of X_g was 7.8% in the 2 wt % VAc solution for a 5-h reaction. X_g in the VAc emulsion was higher than that obtained with the VAc/water solution. On the basis of these results, we can conclude that the emulsion grafting of VAc does not proceed only in an aqueous phase but is also promoted by the VAc micelles.

Grafting of VAc onto the PHB film with VAc/methanol

Previously, an organic solvent such as methanol was used in the grafting reaction.[15] However, the graft reactivity of the VAc monomer was very low, although 100 wt % VAc was used as a monomer solution.

The monomer concentration and grafting reaction time could be changed by control of X_g. Figure 5 shows the effect of the reaction time on X_g when VAc samples with concentrations of 100, 90, and 80 wt % were mixed with methanol and used as solvents. X_g increased with the reaction time until 5 h. X_g decreased from 12 to 6 wt % when the monomer concentration was reduced from 100 to 80 wt % for a 1-h reaction.

Comparison of the grafting efficiency

The grafting reactions were performed with the emulsion, VAc/water, and VAc/methanol solutions. Table III shows the X_g values, weight of graft chains, and grafting efficiency of these systems for 5-h grafting reactions. The grafting efficiency was calculated with the following equation:

$$\text{Grafting efficiency } (\%) = (W_g - W_0)/W_m \times 100$$

where W_g, W_0, and W_m are the weights of the PHB-*g*-VAc film, the PHB film before the grafting reaction, and the VAc monomer in the solution, respectively. $W_g - W_0$ represents the weight of the graft chains.

When 2 wt % VAc monomer solutions were used in the grafting reaction, the grafting efficiencies of the emulsion, VAc/water, and VAc/methanol were 1.01, 0.62, and 0.01, respectively. Thus, it is observed that

TABLE III
Comparison of X_g and Monomer Reactivity with Emulsion, VAc/Water, and VAc/Methanol Solutions

Inclusion	Monomer content (wt %)	Monomer weight (g)	X_g (g)	Weight of graft chains (g)	Grafting efficiency (%)
Water/VAc	1	1.5	2.6	0.0101	0.68
Water/VAc	2	3.0	4.8	0.0187	0.62
Water/VAc/surfactant	2	3.0	7.8	0.0304	1.01
Water/VAc/surfactant	10	15.0	35.0	0.1365	0.91
Methanol/VAc	2	3.0	0.1	0.0004	0.01
Methanol/VAc	80	120.0	9.4	0.0365	0.030
VAc	100	150.0	17.7	0.0689	0.046

the grafting efficiency of the emulsion was approximately 100 times that of VAc/methanol. When VAc/water was used for the grafting reaction, the grafting efficiency was comparatively high, and a maximum X_g of 7.8% was achieved. On the other hand, when the VAc emulsion was used for the grafting reaction, the maximum X_g was 35%. Thus, we can control a wide range of X_g values by emulsion grafting.

CONCLUSIONS

Historically, an organic solvent such as methanol was used for graft reactions of VAc as a solvent. However, graft reactivity was very low when an organic solvent was used. On the other hand, the graft reactivity of VAc was dramatically increased with the introduction of emulsion polymerization. As a result, it succeeded in the establishment of a graft reaction method that could reduce the environmental load.

In this study, PHB-*g*-VAc films were prepared by the preirradiation method with three types of VAc solutions. X_g increased with the reaction time regardless of the type of VAc solution. The maximum X_g achieved was 18% when the VAc concentration was 100%. However, the grafting efficiency was very low. Therefore, when 2 wt % VAc/methanol was used for the grafting reaction, it was observed that only a small amount of VAc was grafted onto the PHB film.

The grafting efficiency was increased significantly to use water as a solvent for the VAc grafting. However, only 2 wt % VAc could dissolve in water, and the maximum X_g was 5% for a 5-h reaction.

When the VAc emulsion was used for the grafting reaction, the maximum X_g achieved was 35%, and the value of the grafting efficiency was the highest. Optimal grafting was achieved when the VAc-to-surfactant ratio in the solution was 10 : 1 (w/w). To achieve grafting with the emulsion solution, the amount of monomer was reduced significantly in comparison with that in the case when VAc/methanol was used. Furthermore, we succeeded in controlling X_g of the PHB-*g*-VAc films. This emulsion grafting method will be made available for many another grafting reactions. However, further research and clarification regarding grafting mechanisms are required.

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