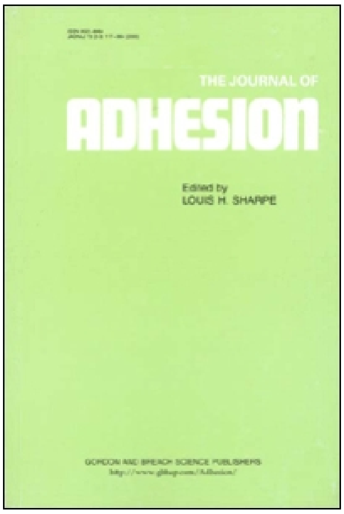

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Dynamic Mechanical Properties and Adhesive Joint Strengths of Emulsion Polymers Produced by Power Feed Technique. II. Chemical Structure of Grafted Power Feed Polymer*

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Power feed copolymers were synthesized using styrene and n-butyl acrylate through a non-uniform feeding emulsion polymerization. Poly(vinyl alcohol) (PVA) was used as a protective colloid, onto which vinyl monomers were grafted. With the increase of PVA, grafting was also increased. Feeding method did not affect grafting nor grafting efficiency to a great extent. However, the amount of initiator had a negative correlation against grafting or grafting efficiency. From NMR spectroscopy, it was known that n-butyl acrylate monomer grafted onto PVA rather than copolymerized with styrene monomer. In order to increase the cohesive strengths of each phase, grafting was introduced to the power feed polymerization. In these cases, the chemical structure of grafted power feed polymer was investigated.

KEY WORDS power feed polymerization; grafting; polyvinyl alcohol; NMR spectroscopy; emulsion polymerization.

INTRODUCTION

In the preceding paper,[1] we demonstrated the dynamic mechanical properties and adhesive joint strengths of power feed emulsion copolymers composed of n-butyl acrylate and styrene or methyl methacrylate. From dynamic mechanical measurement, it was known that the transition peak of a power feed copolymer is very broad. Further, the dynamic mechanical properties of the film cast from solvent after breaking down the emulsion was almost the same as those of the film cast from emulsion. From the above results, we predicted that the system was an alloy

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composed of random copolymers. However, the tensile strengths of the power feed films were very low compared with the corresponding random copolymers, which was attributed to the macrophase separation of the system, *i.e.* the cohesion of the constituent copolymer phases of the power feed copolymer system was low. Because of the low tensile strengths of the films, the adhesive joint strengths were not high. We have shown that the adhesive joint strengths exhibit their maximum around the glass transition temperature.[2-8] If we apply the power feed copolymers as adhesives, they will maintain their adhesive joint strengths in a wide range of temperatures because of their broad transition peak. For that purpose, however, the cohesion strengths of the films must be enhanced.

Poly(vinyl acetate) (PVAc) emulsions are widely used as convenient adhesives, and are particularly good for bonding wood and paper. The emulsion is commonly synthesized by using poly(vinyl alcohol) (PVA) as a protective colloid. Among the aspects specified in our previous papers, the grafting of vinyl acetate monomer onto PVA, which was used as a surfactant at the time of synthesis, was the most significant one.[2-4] We concluded that the higher grafting promoted tight cohesion between PVAc- and PVA-phase after removal of water and enhanced the ultimate strengths of the adhesive film. Furthermore, adhesive joint strengths were also strongly dependent on the tensile strengths of films in accordance with the amount of grafting.

In the present paper, we discuss the chemical structure of power feed copolymers where grafting is introduced using PVA as a protective colloid.

EXPERIMENTAL

Materials

Styrene (St) and n-butyl acrylate (nBA) were used as monomers. Ammonium persulfate (APS) was employed as an initiator. Poly(vinyl alcohol) (PVA) was used as a protective colloid for the emulsion polymerization, of which the degrees of polymerization and of saponification were 1500 and 86.5–89.0 mole%, respectively. All the materials above were purchased from Wako Chemicals Ltd. Aerosol OT (Nakarai Chemicals Ltd.) was used as an anionic surfactant which coexisted with PVA in some cases.

Polymerization

The experimental equipment was shown in the previous paper.[1] Generally, the power feed polymerizations were carried out as follows. First, 650 ml of ion-exchanged water and an appropriate amount of PVA were introduced into the reactor, and the PVA was completely dissolved in the water. 200 ml of St monomer was placed in a far tank and 200 ml of nBA monomer in a near tank. In some cases, we used St in the near tank and nBA in the far tank. The reaction temperature was set at 80–85°C. The required amount of APS as an initiator was dissolved into 50 ml of water and, just prior to the polymerization, 25 ml of the initiation solution was added to the reactor. The rest of the initiation solution was divided into 5 portions and added to the reactor at fixed intervals. The feeding rate of monomers was fixed at $R_1 = 2$ ml/min and $R_2 = 1$ ml/min, so that the feeding of the two kinds of monomers was finished at the same time. The reactor was then maintained at 90°C for two hours. In the cases where the low molecular weight surfactant (Aerosol OT) was used, it was put into the reactor together with the PVA. The preparations of the polymers are summarized in Table I.

After synthesis, the emulsions were cast into film. First, they were left at room temperature for a few days, and then were dried in the oven at 75°C for two days. Before testing, they were vacuum dried for a day at the same temperature.

Calculation of Grafting

The cast films produced as above were extracted with acetone in a Soxhlet extractor for more than 40 hours, and then the residues were similarly extracted with water for the same time. In this way, the original polymers were divided into four polymer fractions, as shown in Figure 1.

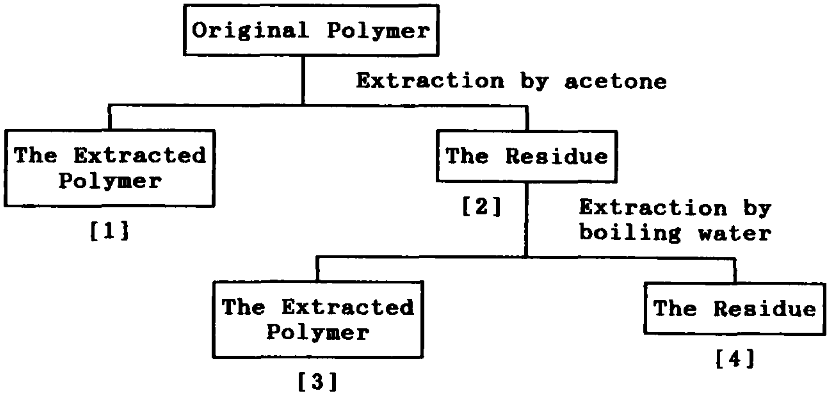
Polymer fraction [1], [2], [3], and [4] obtained by the extraction in Figure 1 were vacuum dried and weighed. Total conversion, grafting, grafting efficiency and grafting efficiency of backbone polymer, which is PVA in this case, were calculated by the following equations.

$$\text{Total conversion} = \frac{\text{Polymerized monomer}}{\text{Total monomers}} \times 100 \qquad (\%)$$

TABLE I
Polymerization recipe and molecular weight distribution of synthesized polymers

No.	Far tank	Near tank	Feeding methods	PVA (g)	APS (g)	Aerosol OT (g)	Mn[d] (X10^{-3})	Mw[e] (X10^{-3})	d[f]
A-1	St	nBA	PF[b]	0	1.0	1.0	124	735	5.9
A-2	(St +	nBA)[a]	Ra[c]	0	1.0	1.0	121	667	5.5
B-1	St	nBA	PF	15.0	1.0	0	91	431	4.7
B-2	St	nBA	PF	15.0	1.0	1.0	56	220	3.9
C-1	St	nBA	PF	17.5	1.0	0	38	176	4.7
C-2	(St +	nBA)	Ra	17.5	1.0	0	36	167	4.7
C-3	St	nBA	PF	17.5	1.0	0.75	136	764	5.6
C-4	St	nBA	PF	17.5	1.0	1.0	140	758	5.4
C-5	(St +	nBA)	Ra	17.5	1.0	1.0	101	524	5.2
C-6	nBA	St	PF	17.5	1.0	1.0	94	443	4.7
D-1	St	nBA	PF	20.0	0.5	0	106	277	2.6
D-2	St	nBA	PF	20.0	1.0	0	77	281	3.7
D-3	St	nBA	PF	20.0	2.0	0	29	167	5.8
D-4	St	nBA	PF	20.0	1.0	1.0	45	417	9.3
E-1	St	nBA	PF	25.0	1.0	0	216	1197	5.5

[a] Parenthesis means monomers were mixed previously
[b] Power feed polymerization
[c] Random polymerization
[d] Number Average Molecular Weight
[e] Weight Average Molecular Weight
[f] Polydispersity



[1] : Copolymers, styrene and n-butylacrylate
[2] : Mixture of graft copolymer and unreacted Poly(Vinyl Alcohol)
[3] : Unreacted Poly(Vinyl Alcohol)
[4] : Pure graft copolymer

FIGURE 1 Polymer Fractions of Emulsion Polymers using PVA as an Emulsifier.

$$\text{Grafting} = \frac{\text{Grafting monomer}}{\text{Backbone polymer}} \times 100 \qquad (\%)$$

$$\text{Grafting efficiency} = \frac{\text{Grafting monomer}}{\text{Polymerized monomer}} \times 100 \qquad (\%)$$

$$\text{Grafting efficiency of backbone polymer} = \frac{\text{Grafted backbone polymer}}{\text{Backbone polymer}} \times 100 \quad (\%)$$

The polymer content in the emulsion can be calcuated by the following equation using the film weight after drying.

$$\text{polymer content} = \frac{(\text{total monomer} \times \text{conversion})/100 + \text{backbone polymer}}{\text{water} + \text{backbone polymer} + \text{total monomers}} \times 100$$

Measurement of Molecular Weight by GPC

Polymer fractions [2], [3], and [4] were not soluble in acetone or tetrahydrofuran (THF) because PVA was present. But polymer fraction [1] did dissolve in THF, so that its molecular weights were estimated by gel permeation chromatography, using an ALC/GPC 501 (Waters Associates) instrument with refractive index detector. Column set and solvent condition were as follows: μ-styragel 10^6, 10^5, 10^4, 10^3 Å with THF 2 ml/min. The molecular weight distributions were calculated from the calibration curve obtained by the use of polystyrene standards.

Analysis of Chemical Structure

The sequence distributions of polymer fraction [1] of emulsion copolymers coexisting in the system of PVA and surfactant were examined by using ^{13}C-NMR. In addition, the sequence distributions of polymers which was synthesized in a single surfactant system were also examined. The sequence distributions were analyzed using the carbonyl carbon of nBA. The NMR used was an FX-100 (JEOL) instrument, at a frequency of 25.0 MHz, pulse interval of 2 seconds and flip angle of 45°. The solvent and the internal standard were chloroform-d_1 and tetramethylsilane, respectively.

RESULTS AND DISCUSSION

Relation Between Grafting and Other Factors

In the case of emulsion polymerization using PVA as a protective colloid, vinyl monomers are easy to graft onto PVA as well as to homopolymerize. Figure 2 shows how the grafting reaction occurs. Generally, it is considered that the grafting reaction takes place not through the chain transfer of a homopolymer radical to the backbone polymer, but through the chain transfer of the initiator radical to the backbone polymer. Grafting in the power feed emulsion polymerization can be controlled by the following factors; a) feeding methods; b) protective colloids and surfactants; c) initiators; d) other conditions. Table I shows the polymerization recipe and molecular weight distributions of polymer fraction [1], and Tables II–V show the grafting ratio as a function of various factors. Table II shows total conversions, grafting, and grafting efficiencies against feeding method, the values of which were almost the same when the other conditions were equal. So it can be said that feeding method does not affect grafting to a great extent.

It is known that the grafting efficiency generally increases as the concentration of the backbone polymer increases. This was confirmed in the single emulsifier system

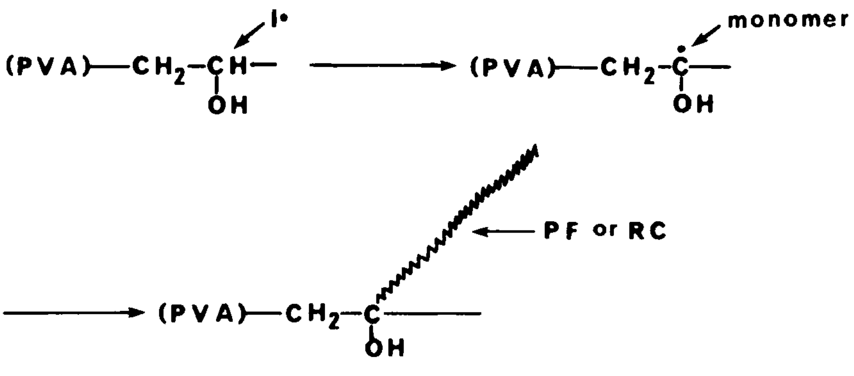


FIGURE 2 Grafting Reaction of Power Feed Copolymer (PF) or Random Copolymer (RC) onto PVA.

TABLE II
Grafting of emulsion polymers vs. feeding method

No.	Far tank	Near tank	Feeding methods	Polymer content	Total conversion	Grafting	Grafting efficiency	Grafting efficiency of backbone polymer
A-1	St	nBA	PF	33.5	98.0	—	—	—
A-2	(St	+nBA)	Ra	33.7	98.6	—	—	—
C-1	St	nBA	PF	32.2	91.3	688	36.5	51.0
C-2	(St	+nBA)	Ra	32.3	91.4	606	32.1	60.2
C-4	St	nBA	PF	33.7	95.7	630	32.0	45.7
C-5	(St	+nBA)	Ra	34.6	98.1	683	33.5	48.8
C-6	nBA	St	PF	33.9	96.3	777	39.2	45.9

TABLE III
Grafting of emulsion polymers vs. protective colloid

No.	Existence of A-OT	Amounts of PVA (g)	Polymer contents	Total conversion	Grafting	Grafting efficiency	Grafting efficiency of backbone polymer
B-1	No	15.0	33.8	96.5	147	6.3	—
C-1	No	17.5	32.2	91.3	688	36.5	51.0
D-2	No	20.0	36.0	100	727	39.4	52.2
E-1	No	25.0	34.4	96.5	659	47.2	48.6
A-1	Yes	0	33.5	98.0	—	—	—
B-2	Yes	15.0	27.3	77.1	913	49.1	67.6
C-4	Yes	17.5	33.7	95.7	630	32.0	45.7
D-4	Yes	20.0	35.5	100	685	37.8	38.8

TABLE IV
Grafting of emulsion polymers vs. surfactant

No.	Amounts of A-OT (g)	Amounts of PVA (g)	Polymer contents	Total conversion	Grafting	Grafting efficiency	Grafting efficiency of backbone polymer
B-1	0	15.0	33.8	96.5	147	6.3	—
B-2	1.0	15.0	27.3	77.1	913	49.1	67.6
C-1	0	17.5	32.2	91.3	688	36.5	51.0
C-3	0.75	17.5	33.4	96.2	674	33.9	74.6
C-4	1.0	17.5	33.7	95.7	630	32.0	45.7
D-2	0	20.0	36.0	100	727	39.4	52.2
D-4	1.0	20.0	35.5	100	685	37.8	38.8

TABLE V
Grafting of emulsion polymers vs. amounts of initiator

No.	Amounts of APS (g)	Polymer contents	Total conversion	Grafting	Grafting efficiency	Grafting efficiency of backbone polymer
D-1	0.5	29.2	81.7	662	44.8	41.9
D-2	1.0	36.0	100	727	39.4	52.2
D-3	2.0	38.5	100	681	34.4	47.0

of PVA as shown in Table III. However, in the case with a coexistent surfactant, there was no relationship between the amount of PVA and grafting efficiency.

In Table IV, we show the grafting of emulsion polymers against surfactant. As the content of surfactant increased, the grafting efficiency decreased to some extent.

From Table V, it is seen that there is a negative correlation between the grafting or grafting efficiency and the amount of APS. Although it is generally said that the grafting and grafting efficiency increase with the concentration of APS,[9] we did not observe the above fact in the present work. However, there is a study in the literature which shows that grafting and grafting efficiency decrease with the increase of APS in the case of emulsion polymerization of vinyl acetate.[3]

We assume that polymer fraction [4] is a graft copolymer of St-nBA copolymers grafted onto PVA, because it was neither soluble in acetone nor water. However, if a crosslinking reaction had occurred, the polymer will also not dissolve in either acetone or water. In order to confirm our assumption, we dissolved the polymer fraction [4] in dimethyl sulfoxide (DMSO), which is a solvent common to PnBA, PSt and PVA. After two days, the polymer was completely dissolved in DMSO. Therefore, we concluded that the residue of the extractions, polymer fraction [4], was a graft copolymer.

Analysis of the Chemical Structure of the Graft Copolymers by ^{13}C-NMR

a) Sequence Distribution Difference due to Feeding Method The ^{13}C-NMR spectra were measured using homopoly(n-butyl acrylate), as well as the acetone soluble parts (polymer fraction [1]) of C-4, C-5, and C-6 in order to clarify the sequential distributions of grafted polymer. The spectra of the above 4 samples are shown in Figure 3.

The signals of carbonyl carbon of nBA appear at the low magnetic field from 173ppm to 177ppm. Homo-PnBA has one signal at 174ppm. According to the literature,[10] three kinds of triads, B/B/B, B/B/S or S/B/B, and S/B/S (B:nBA, S:St), have signals of this order from the higher magnetic field. So, from the intensity, the sequential distributions can be known. We named these three signals I, II, and III from the higher magnetic field. In Table VI the relative intensities due to the triads are shown, the sum of which was made to equal 100. The average sequence lengths of nBA were calculated by the following equation.

$$\text{Average Sequence Length} = \frac{\mathrm{I} + \mathrm{II} + \mathrm{III}}{\mathrm{III} + \mathrm{II}/2}$$

In the case of emulsion polymer C-6, St is rich at the early stage of polymerization; a large amount of III (S/B/S), however, was detected. This fact means that nBA grafts more easily than St onto PVA.

b) Sequence Distribution Difference due to Reaction Time During the reaction of A-1, samples were taken from the reactor three times. These were made into films at room temperature. The above three polymers were then analyzed by ^{13}C-NMR. The spectra of the carbonyl carbon of nBA are shown in Figure 4, where it is clear that copolymers of St and nBA are increasing with time. As above, the ratio among

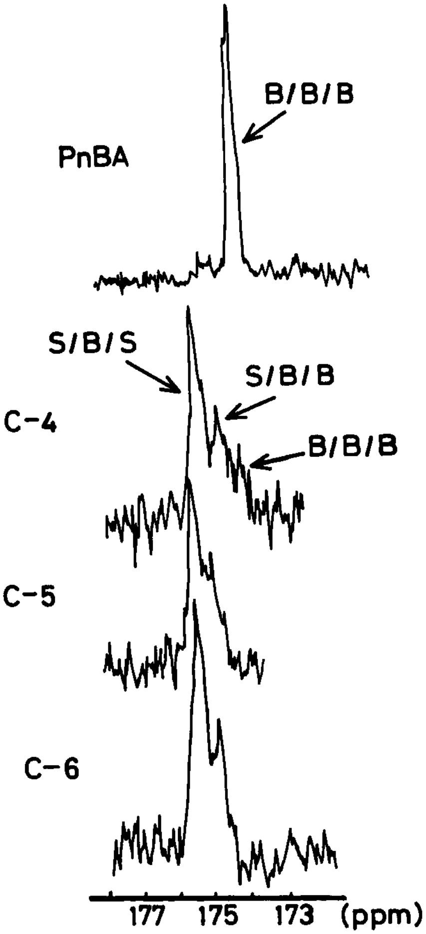


FIGURE 3 ^{13}C-NMR Spectra for Emulsion Polymers Made Using Different Feeding Methods.

TABLE VI
Sequential distributions and average sequence lengths vs. feeding methods

No.	I	II	III	Average sequence length
C-4	12.4	31.0	56.6	1.4
C-5	0	46.4	53.6	1.3
C-6	0	21.0	79.0	1.1

TABLE VII
Sequential distributions and average sequence lengths vs. reaction times

Time (min.)	I	II	III	Average sequence length
60	79.8	20.2	0	5.0
150	43.8	38.2	18.0	2.7
320	30.1	26.0	43.9	1.8

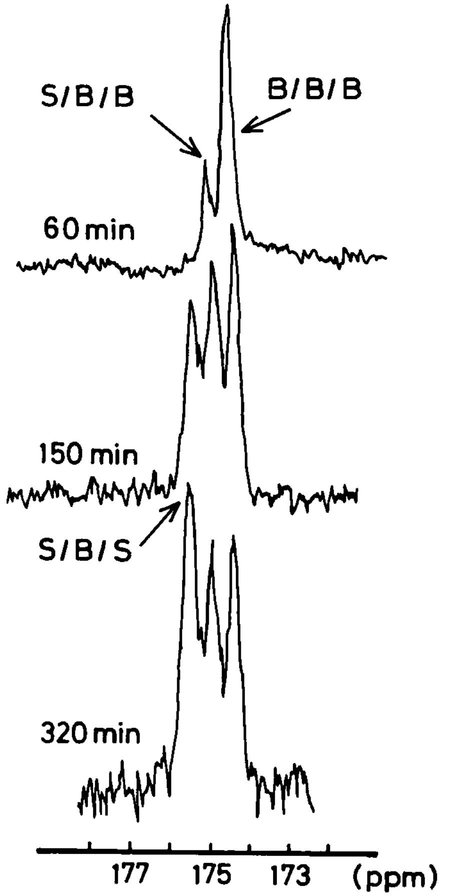


FIGURE 4 ^{13}C-NMR Spectra for Power Feed Polymer Made Using Different Reaction Times.

I, II, and III and the average sequence length were calculated and the results are shown in Table VII. Although I (B/B/B) was hardly detected from the results given in Table VI, some I is evident in Table VII. This proves that nBA, which is more reactive than St, has a longer sequence length, and grafts faster onto PVA, than St. It is presumed that the grafting of nBA onto PVA gradually comes to a halt in the late stages of polymerization.

CONCLUSIONS

Power feed copolymers were synthesized using non-uniform feeding emulsion polymerization. Polyvinyl alcohol (PVA) was used as a backbone polymer onto which vinyl monomers were grafted. With the increase of PVA, grafting was also increased. Neither feeding method nor amount of initiator affected grafting or grafting efficiency to a large extent. The original polymer was divided into 4 polymer fractions, using a Soxhlet extractor, in order to confirm the grafting reaction. From NMR spectroscopy, it was shown that n-butyl acrylate monomer preferred to graft onto PVA rather than to copolymerize with styrene monomer.

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