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ORIGINAL CONTRIBUTION

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Radical graft polymerization onto composite particles of polydimethylsiloxane and polybutadiene

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Abstract Submicron-size composite polymer particles consisting of polydimethylsiloxane/core and polybutadiene/shell were synthesized by seeded emulsion polymerization. The morphologies of composite particles were affected by polybutadiene ratio in the composite particles. Highly grafted polymer by poly(styrene-*co*-acrylonitrile) could be prepared by using the composite particles containing polybutadiene with polymerizable group. The morphologies of the grafted polymer were influenced by the morphologies of composite particles and the kinds of grafting initiators. It was found that surface gloss and lubricity of the graft polymers were influenced by morphologies of composite particles.

Key words Composite polymer particles – polydimethylsiloxane – polybutadiene – graft polymerization – morphology

Introduction

Polydimethylsiloxane (PDMS) is an extremely interesting material with excellent properties such as lubricity, water repellency, heat resistance, weather resistance and high oxygen permeability. Therefore, PDMS has been the subject of numerous studies because of many application of this material. From the academic point of view, the interest has been mainly due to functional organic materials with properties of both PDMS and another polymer [1–11]. To extend the use of PDMS in various fields of science and technology, it is particularly advantageous to graft different polymers onto PDMS because this graft polymer shows the independence behavior of the backbone part and graft part.

To prepare the graft polymer, macromolecular monomers with polymerizable functional groups under the trade name MACROMERS were proposed in 1974 [12]. Since then, MACROMERS have received much attention from synthetic polymer chemists and many new graft polymers have been prepared by using MACROMERS. Graft polymer containing PDMS could be prepared also by using PDMS with functional groups such as mercaptopropyl group [1], methacryloyl group [5, 13, 14], silyl vinyl group [6], styryl group [15, 16], allyl group [16], and hexenyl group [16].

On the other hand, we have recently reported novel grafting method of styrene and acrylonitrile onto silylmethyl group of PDMS without functional group. Grafted polymer was consequently obtained by selection of adequate initiator; *tert*-butyl perlaurate coupled with ferrous sulfate [17]. The goal of this research is to prepare grafted polymer containing PDMS without functional group.

This paper elaborates on how highly grafted polymer by poly(styrene-*co*-acrylonitrile) (SAN) could be prepared by using composite particles of PDMS/core (without functional groups) and polybutadiene (PB)/shell (with double bond in the polymer main chain) as seed particles. Furthermore, surface gloss and lubricity of the grafted polymers are also discussed.

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Experimental

Materials

Octamethylcyclotetrasiloxane (Toshiba Silicone), methyltriethoxysilane (Toshiba Silicone), *n*-dodecylbenzenesulfonic acid (Kao), butadiene (Japan Synthetic Rubber), styrene (Mitsubishi Chemical), acrylonitrile (Mitsubishi Chemical), potassium laurate (Nippon Oil and Fats), diisopropylbenzene hydroperoxide (DHP, Nippon Oil and Fats), *tert*-butyl hydroperoxide (BHP, Nippon Oil and Fats), and sodium carbonate (Asahi Chemical) were commercial products and used directly without purification. Potassium persulfate, iron(II) sulfate heptahydrate, dextrose sodium pyrophosphate and toluene were purchased from Wako Pure Chemical Industry, and used without further purification. Poly(styrene-*co*-acrylonitrile)-*g*-polybutadiene (ABS, #630A, PB content: 35 wt%) and poly (styrene-*co*-acrylonitrile) (SAN, #290NC, AN content: 25 wt%) were commercial grade of Japan Synthetic Rubber Co. Ltd. Polyoxymethylene (POM, #SW-01) was the commercial high lubricity grade of Polyplastic Co. Ltd.

Preparation of PDMS latex

PDMS latex was prepared by cationic polymerization of octamethylcyclotetrasiloxane initiated by *n*-dodecylbenzenesulfonic acid by using conditions described previously [18]. Table 1 indicates a polymerization recipe. Polymerization was quenched by neutralization of the addition of sodium carbonate. The average particle size showed 0.17 μm by transmission electron micrograph (TEM). The percentage of insoluble polymer part in toluene was 57%.

Preparation of the composite particle

Composite particles were prepared by emulsifier-free batch-seeded emulsion polymerization for butadiene with PDMS seed particle. Polymerization were carried out in a 300 ml high-pressure bottle. The typical reaction recipe and reaction conditions are given in Table 2. PDMS latex and sodium persulfate solution were added to the reactor, and the bottle was capped and evacuated. Butadiene was charged to the reactor and the system had been aging at 60–70 °C for 48 h. The remainder (50%) of potassium persulfate solution was boosted to the reactor at the middle of whole reaction time. After polymerization, the latex of composite particles was kept for 4 h at 70 °C under nitrogen bubbling to evaporate butadiene unreacted. The percentage of insoluble polymer part in toluene was 88%. The soluble polymer part in toluene consisted of uncross-linked PDMS and uncross-linked PB.

Table 1 The conditions used in the preparation of the PDMS latex

Octamethylcyclotetrasiloxane	(g)	288
Methyltriethoxysilane	(g)	12
Deionized water	(g)	450
93% *n*-dodecylbenzenesulfonic acid	(g)	6.45
Particle size[a)]	(μm)	0.17
Insoluble polymer part in toluene	(%)	57

[a)] Determined by TEM.

Preparation of the graft polymer

Table 3 indicates a typical graft polymerization recipe. The method used to generate free radicals was used redox

Table 2 The conditions used in the preparation of the composite particles of PDMS/core and PB/shell

35% PDMS latex	(g)	143
Butadiene	(g)	50
3% potassium persulfate	(g)	33
Particle size[a)]	(μm)	0.25
Insoluble polymer part in toluene	(%)	88

[a)] Determined by TEM.

Table 3 The conditions used in the preparation of the graft polymer particles

Ingredients		
Batch polymerization		
40% composite polymer latex	(g)	300
30% potassium laurate	(g)	5.4
Deionized water	(g)	180
Styrene	(g)	26
Acrylonitrile	(g)	10
57% diisopropylbenzene hydroperoxide	(g)	0.94
The reductant solution		
Iron(II)sulfate heptahydrate	(mg)	12
Dextrose	(g)	0.75
Sodium pyrophosphate	(g)	0.6
Deionized water	(g)	25
Semi-continuous polymerization		
Deionized water	(g)	100
30% potassium laurate	(g)	11
Styrene	(g)	100
Acrylonitrile	(g)	41
57% diisopropylbenzene hydroperoxide	(g)	0.47
Boost polymerization		
57% diisopropylbenzene hydroperoxide	(g)	0.47
The reductant solution		
Iron(II)sulfate heptahydrate	(mg)	3
Dextrose	(g)	0.25
Sodium pyrophosphate	(g)	0.2
Deionized water	(g)	8.3

reaction between organic peroxide and ferrous sulfate. The graft polymer latexes were prepared by batch and semi-continuous emulsion polymerization. The reactor consisted of 1 l separable flasks equipped with ports for nitrogen, a condenser, a dual four-bladed marine-type propeller, an alcohol thermometer and a monomer introduction. The composite polymer latex as seed and deionized water were charged to the reactor, followed by potassium laurate. The stirring was effected by the stirrer with downward flow at 100 rpm. All reactions were carried out in a water bath kept at constant temperature of 70 °C. Before polymerization, the reaction system was purged with nitrogen, and a small positive pressure of nitrogen was maintained during the reaction. After the internal temperature of the reaction system was raised to 70 °C, batch styrene and acrylonitrile, diisopropylbenzene hydroperoxide and the reductant solution (iron(II) sulfate heptahydrate, dextrose and sodium pyrophosphate) were added. After the percentage of batch monomer conversion calculated from the total solid concentration was beyond 80%, the monomer emulsifier with initiator (styrene, acrylonitrile, deionized water, potassium laurate and diisopropylbenzene hydroperoxide solution) was added continually at a constant rate for 4 h using a syringe pump. Finally, diisopropylbenzene hydroperoxide and the reductant solution were added to the stirred solution, and the reaction was continued for 1 h. The polymers were coagulated by pouring this latex into hot water with 2 parts of dissolved calcium chloride. After washing by water several times, the polymers were dried at 75 °C for 12 h.

Graft ratio of the polymer

Graft ratio of the polymer was measured according to the method described in the literature [1] (solvent extraction by acetone; a solvent for SAN but not for the composite particle). The graft ratio was calculated as follows:

$$\text{Graft ratio (\%)} = (W_1 - W_0)/W_0 \times 100 ,$$

where W_0 is the initial weight of the composite particle and W_1 is the weight of grafted SAN plus initial weight of the composite polymer.

Preparation of test samples of grafted polymer

The blends prepared by mixing SAN (60 wt%) with the raw product of graft polymer (40 wt%) were molded with twin screw extruder at 230 °C. The test samples for measuring surface gloss and sliding wear resistance were obtained by injection molding of the blends at 230 °C.

Surface gloss of the polymer

Surface gloss of the polymer was measured according to ASTM D-523 (the reflection angle was 45°).

Sliding wear resistance of the polymer

Sliding wear resistance of the polymer was measured according to JIS K7218 (A-method). In the sliding test, a Suzuki-system sliding tester (ORIENTIC, MODEL: EMF-III-EN Friction and Wear Tester) was used, and a steel (S45C) was used as a countermember. The test piece was a hollow cylinder with an outer diameter of 25.6 mm and an inner diameter of 20.0 mm. The surface of the steel was ground by sandpaper (#600), washed by acetone and dried before use. The conditions for measurements of the friction coefficient and the wear were as follows. The load was 2.0 kg, the running speed was 500 mm/s and running distance was 3 km at room temperature and 50% humidity.

Results and discussion

Preparation of composite particle

Submicron-size composite polymer particles of PDMS/core and PB/shell were prepared by emulsifier-free seeded emulsion polymerization for butadiene with PDMS seeded particles. The results are summarized in Table 4. TEM of latexes are shown in Figs. 1 and 2. These latexes were stained by osmic acid for definition. The white and black regions in particles shows PDMS and PB, respectively. Composite particles consisting of PDMS/core and PB/shell could be synthesized without new PB particles. When PB ratio in composite particles was low (up to 26%), morphologies of composite particles were crescent moon structure as shown in Fig. 1. On the other hand, when PB ratio was high (43%), that was complete core-shell structure as seen in Fig. 2.

From these results, the mechanism of the formation of composite particles are proposed as shown in Scheme 1. At the first stage (before polymerization), it is thought that butadiene is absorbed and swelled in PDMS seed particles because butadiene's solubility parameter value is close to PDMSs [19]. At the second stage, PB migrates to the surface of PDMS particles through polymerization. Phase separation between PDMS and PB in composite particles can be explained as follows: (1) As summarized in Table 5, this morphology is thermodynamically stable, because free energy for forming core-shell composite particles becomes very small [20–22]. γ_{A-B} is interface free energy of the two

Table 4 Effect of PB ratio in composite particles on the properties of the composite particles

Sample	Composition PDMS/PB	Diameter (μm)[a]		Insoluble polymer part (%)	Morphology	
		Inner	Outer		Type	Figure
1	100/0	0.17	—	57	—	—
2	94/6	—	0.19	—	Crescent moon	—
3	88/12	—	0.22	71	Crescent moon	—
4	82/18	—	0.22	76	Crescent moon	Fig. 1
5	74/26	—	0.23	—	Crescent moon	—
6	57/43	0.17	0.25	88	Complete core shell	Fig. 2

[a] Determined by TEM.

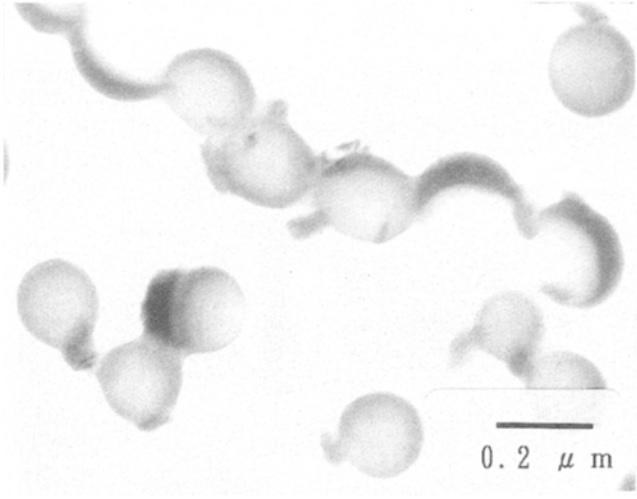


Fig. 1 TEM of composite particles of PDMS/core and PB/shell (Sample 4, Table 4)

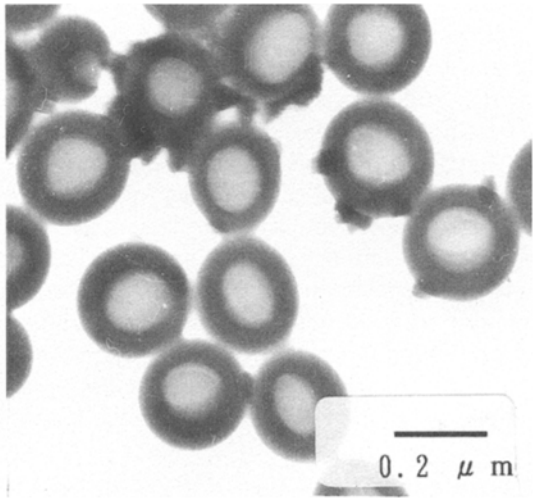
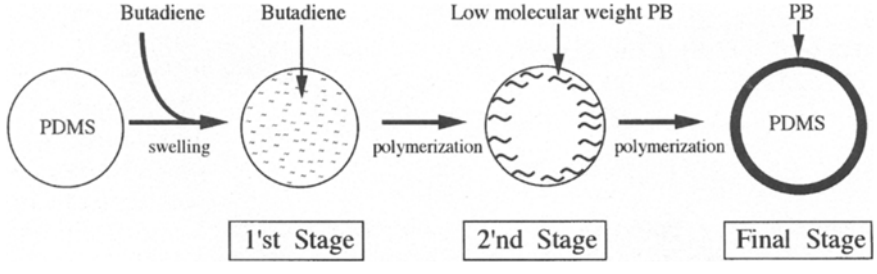


Fig. 2 TEM of composite particles of PDMS/core and PB/shell (Sample 6, Table 4)

Scheme 1 Schematic presentation of the formation mechanism of composite particles consisting of PDMS/core and PB/shell



polymers A and B; $\gamma_{C-water}$ is the interface free energy of the initial latex particles against water. $\gamma_{B-water}$ and $\gamma_{A-water}$ are the interface free energies of polymer A against water and polymer B against water, respectively. (2) There is no chemical bond between PDMS and PB because potassium persulfate which was used in preparation for the composite particles could not abstract hydrogen atom of PDMS. In the final stage, complete core-shell structure particles were prepared by forming the cross-linked PB/shell.

Preparation of graft polymer particles

Figure 3 shows the relationship between graft ratio and PB ratio in the seeded latex. Graft polymerization onto

Table 5 Interface free energy of polymer to water

Sample	Solubility parameter [19]	Contact angle for water θ	$\gamma_{polymer-air}$ [a] (10^{-3} J/m^2)	$\gamma_{polymer-water}$ [b] (10^{-3} J/m^2)	ΔG [c] (10^{-3} J/m^2)
PDMS	7.0	128	2.69	47.5	0
Butadiene	7.1	–	–	–	–
PB	8.4	107	9.11	30.4	−17.1

[a] $\gamma_{polymer-air}$ was calculated according to the following equation [21]: $\gamma_{polymer-air} = \gamma_{water-air} \times (1 + \cos\theta)^2/4$, where $\gamma_{polymer-air}$ and $\gamma_{water-air}$ are the surface free energy of polymer and water, respectively.

[b] $\gamma_{polymer-water}$ was calculated according to the following Young's equation: $\gamma_{polymer-water} + \gamma_{water-air}\cos\theta = \gamma_{polymer-air}$.

[c] ΔG was calculated according to the following equation [22]: $\Delta G = (-\Delta G_{core-shell}) - (-\Delta G_{invert}) = (\gamma_{A-B} + \gamma_{B-water} - \gamma_{C-water}) - (\gamma_{A-B} + \gamma_{A-water} - \gamma_{C-water}) = \gamma_{B-water} - \gamma_{A-water}$.

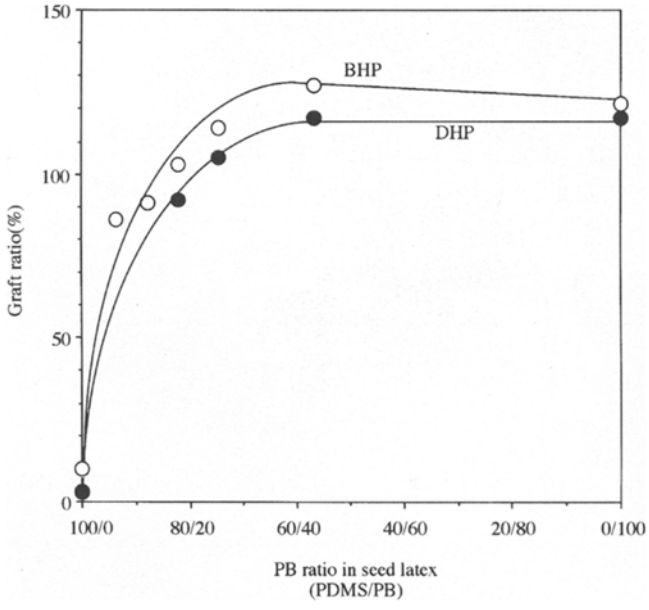


Fig. 3 Relationship between PB ratio in seed latex and graft ratio of grafted polymer by SAN

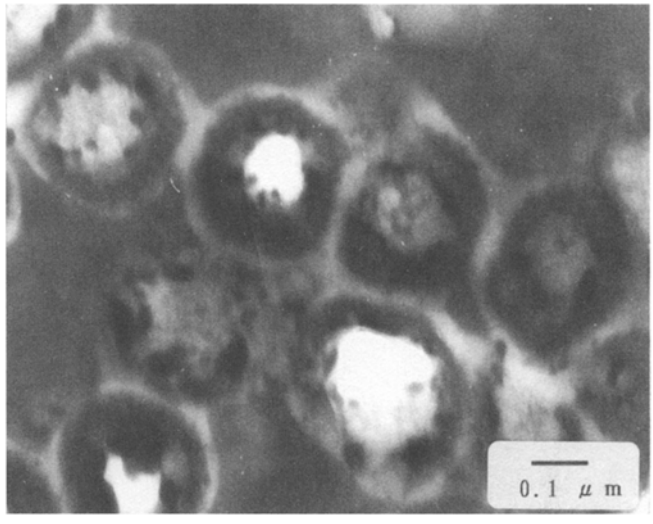


Fig. 4 TEM of graft polymer particles (Sample A, Table 6)

PDMS particles scarcely progressed by using common initiators such as DHP and BHP. This reason is due to the fact that the reaction activity of polymeric free radical is very small at the site of silylmethyl group of the PDMS [23]. However, graft polymerization progressed dramatically by using the composite particles. The reason could be the following: (1) α-hydrogen atom of cis or trans PB that is abstracted easily by oxyradical is about 400 times as that of methyl groups of PDMS [24]. (2) PB contains vinyl microstructure about 20 mol% [25]. (3) PB/shell layer exists at the surface of the composite particles as the site of graft reaction.

Morphologies of graft polymer particles

TEM of graft polymer particles are shown in Figs. 4–6. To clarify the graft layer of SAN on composite particles, graft polymer particles were protected by epoxy resin and stained by osmic acid. The white regions around the particles shows graft layer of SAN. The morphologies of graft polymer particle are summarized in Table 6. When graft polymer particle was synthesized in the presence of composite particles of complete core-shell structure as a seed latex by using DHP which has scarcely grafting ability onto PDMS, good coverage of SAN onto the composite particles was achieved (Fig. 4). The thickness of SAN of graft layer was about 0.03 μm. Therefore, each graft polymer particle exists independently without coalescence of the particles. This PDMS/core-PB/shell-SAN/shell morphology is thermodynamically stable because free energy for forming this

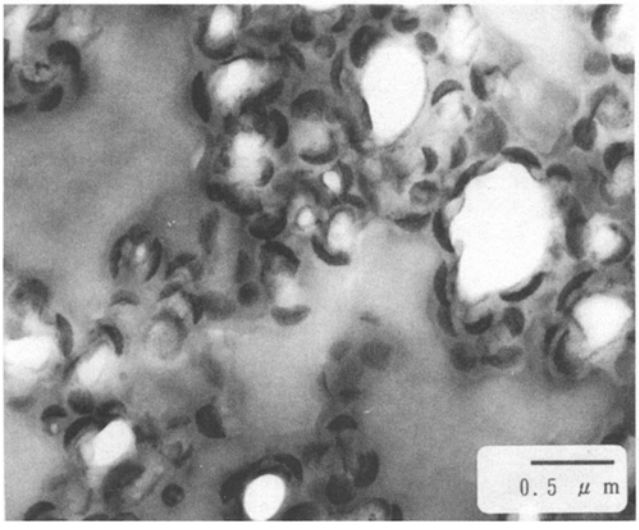


Fig. 5 TEM of the graft polymer particles (Sample B, Table 6)

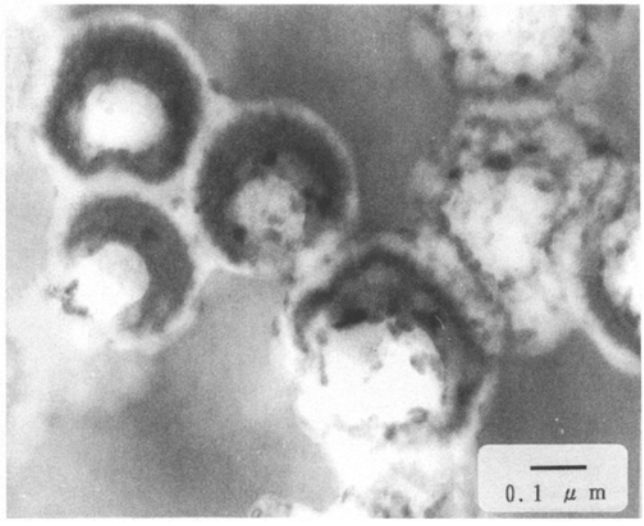


Fig. 6 TEM of the graft polymer particles (Sample C, Table 6)

Table 6 Effect of the kinds of composite particles and grafting initiator on properties of graft polymer particles

Graft polymer particles	Seed composite particle		Diameter (μm)[a]			Grafting initiator	Graft ratio (%)	Figure of morphology
	Sample	Figure	Core	Shell	Grafted			
A	6	Fig. 2	0.17	0.25	0.32	DHP	117	Fig. 4
B	4	Fig. 1	0.17–0.50	0.26–0.70	0.30–0.80	DHP	92	Fig. 5
C	6	Fig. 2	0.17	0.25	0.32	BHP	127	Fig. 6

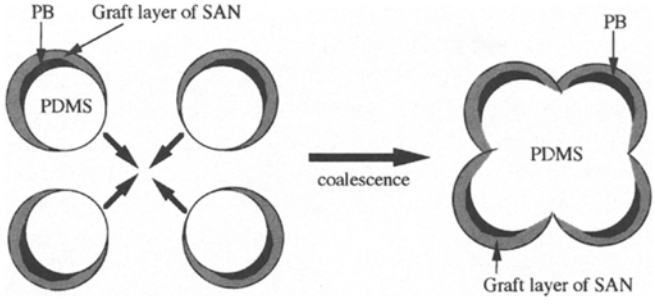
[a] Determined by TEM.

Table 7 Interface free energy of polymer to water[a]

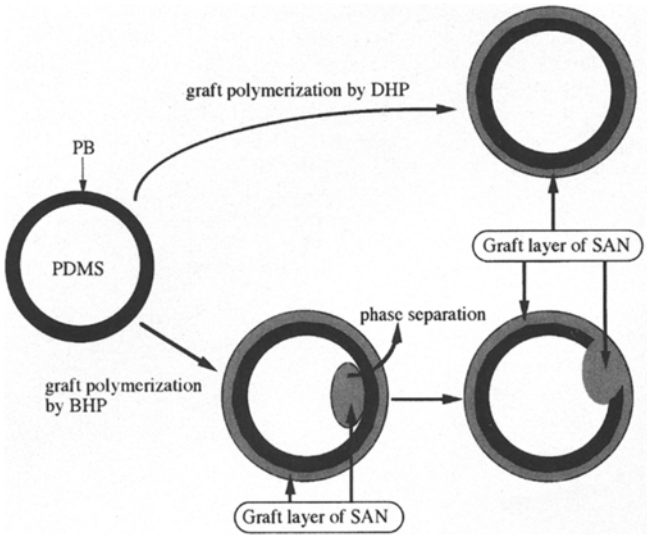
Sample	Contact angle for water θ	$\gamma_{polymer-air}$ (10^{-3} J/m^2)	$\gamma_{polymer-water}$ (10^{-3} J/m^2)	ΔG (10^{-3} J/m^2)
PB	107	9.11	30.4	0
SAN	68	34.4	7.12	− 23.3

[a] Calculated in the same manner described in Table 5.

structure becomes small as shown in Table 7. On the other hand, complete coverage of SAN onto the composite particles could not be accomplished by using composite particles of crescent moon structure. Therefore, the coalescence of graft polymer particles was observed as shown in Fig. 5. The mechanism of the coalescence is proposed as shown in Scheme 2. When graft polymer particle was synthesized by BHP as a grafting initiator, the fracture of PB/shell was observed as shown in Fig. 6. The reason that as grafting reactivity of BHP onto PDMS is higher than that of DHP, graft polymerization progress at the site of both PB/shell layer and PDMS/core part of the composite



Scheme 2 The schematic presentation of the coalescence mechanism of the graft polymer particles



Scheme 3 The schematic presentation of the formation mechanism of graft polymer

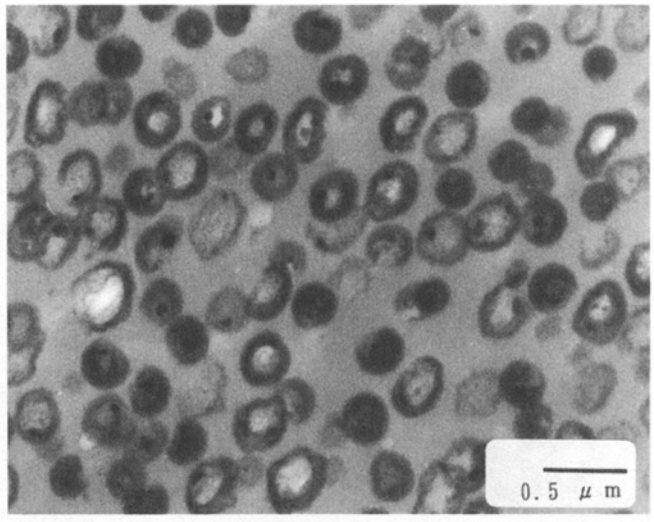


Fig. 7 TEM of the graft polymer particles (Sample A, Table 6) stained by osmic acid. Composition of compound: graft polymer/SAN = 40/60

Table 8 Properties of the graft polymer particles[a] and other resins

Graft polymer particles	Surface gloss (%)	Lubricity	
		Coefficient of friction (μ)	Wear (mg)
A	86	0.31	3.2
B	26	0.18	0.5
C	84	0.19	0.8
ABS	85	0.45	25
POM	34	0.20	1.2

[a] Composition: graft polymer/SAN = 40/60 (wt%) and rubber content was 16 wt%.

particles, SAN-g-PDMS is migrated to the composite particle surface by phase separation through the fracture of PB/shell. The schematic presentation of grafting mechanism is illustrated in Scheme 3.

Practical properties of the graft polymer

Practical properties of the graft polymer are summarized in Table 8. High surface gloss could be accomplished by the homogeneous submicron-size disperson of graft polymer particles in SAN matrix as shown in Fig. 7 (sample A). On the other hand, low surface gloss of the sample with composite particles of crescent moon structure is due to the rough surface caused by the existence of large-sized polymer particles whose wavelength is larger than the wavelength of visible spectrum (sample B) [26, 27]. Good lubricity could be also achieved by PDMS direct exposure in SAN matrix caused by destruction of PB/shell (sample C).

Acknowledgments We thank Mr. K. Hirose for measurements of the morphologies.

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