

Synthesis of Poly(tetrafluoroethylene)/Poly(butadiene) Core-Shell Particles and Their Graft Copolymerization

MOTOKI OKANIWA

Tsukuba Research Laboratory, JSR Corporation, Ltd., 25 Miyukigaoka, Tsukuba, Ibaraki 305-0841, Japan

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ABSTRACT: This article describes how to convert the unreactive surface of poly(tetrafluoroethylene) (PTFE) into poly(styrene-*co*-acrylonitrile) (SAN). Composite particles with a crosslinked poly(butadiene) (PB) shell covered over a PTFE core were prepared by an emulsifier-free seeded emulsion polymerization of butadiene in the presence of PTFE latex. It was found that the increase in the PB crosslink density resulted in depressing the formation of PB secondary particles. Then, styrene and acrylonitrile were able to graft onto PB shell in high efficiency of 70%. SAN-modified PTFE/PB core-shell particles could eventually be dispersed homogeneously in a SAN matrix. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 185–190, 1998

Key words: composite polymer particles; poly(tetrafluoroethylene); poly(butadiene); graft polymerization; morphology; core-shell

INTRODUCTION

Over the last half century, poly(tetrafluoroethylene) (PTFE) has become one of the world's most important commodity plastics because of its heat resistance, high toughness at a low temperature, chemical resistance, lubricity, characteristic electric properties, etc.¹ Most of these properties are attributed to low polarizability of the C—F bonds. The hydrophobic surface of PTFE is a distinguishing characteristic but brings a difficulty for adhesion with other materials. Many investigators have studied surface modifications of PTFE using chemicals, grafting, sputtering, and plasma treatments.² Initiation of a substitution reaction is not easy because of the high bond energy of the C—F bond (486 kJ/mol), therefore, requiring highly reactive chemicals (e.g., sodium naphthalene complex) or high energy input (e.g., plasma).^{3,4}

On the other hand, emulsion polymerization methods employ various possibilities to prepare

particles with controlled morphologies and surface properties. In addition, it is well known that the emulsion polymerization does not require high energy and offers an efficient opportunity for an industrial scale production. The core-shell arrangements provided by the emulsion polymerization technique meet many requirements in particle applications. For instance, we demonstrated that graft copolymerization of styrene and acrylonitrile onto inert poly(dimethylsiloxane) (PDMS) was accomplished with composite particles possessing PDMS/core and poly(butadiene) (PB)/shell architecture⁵ or by a selected radical initiator.⁶

As a result of further investigations about the shell coating and grafting reaction, I found that surface of PTFE was also able to be modified on demand. This article describes how to convert the unreactive surface of PTFE into poly(styrene-*co*-acrylonitrile) (SAN). Composite particles with a crosslinked PB shell covered over a PTFE were prepared by an emulsifier-free seeded emulsion polymerization of butadiene with PTFE seeded particles. Then, SAN was successfully grafted

onto PB shell in high efficiency of 70%. SAN-modified PTFE/PB core-shell particles could be dispersed homogeneously in a SAN matrix, eventually.

I believe that this method can be widely applied to modify any particles with an inert surface as well as PTFE and PDMS. Dispersing PTFE particles may bring characteristic properties of PTFE: low dielectric permeability, low refractive index, into the matrix. Such new composite materials may offer interesting possibility as applications in electronics and optics.

EXPERIMENTAL

Materials

PTFE Latex was a commercial grade from Hoechst Industry Co., Ltd. (Hostafon, 5032, Lot. No 33-48084). Particle average diameter of the latex determined by transmission electron micrograph (TEM) was 0.16 μm . The insoluble PTFE in toluene was 100%. Styrene (Mitsubishi Chemical), acrylonitrile (Mitsubishi Chemical), potassium laurate (Nippon Oil and Fats), and diisopropylbenzene hydroperoxide (DHP, Nippon Oil and Fats) were commercial products and used directly without purification. Potassium persulfate, iron(II) sulfate heptahydrate, dextrose sodium pyrophosphate, *tert*-dodecanetriol, toluene, and 2-butanone were purchased from Wako Pure Chemical Industry, and used without further purification. Butadiene and SAN (No. 29 ONC; AN content 25%) were commercial grade from JSR Corporation.

Preparation of the PTFE/PB Core-Shell Composite Particles

The PTFE/PB core-shell particles were prepared by emulsifier-free batch seeded emulsion polymerization of butadiene with a PTFE seed particle. Polymerization was carried out in a 300-mL high-pressure bottle. PTFE latex (60%) (41.7 g), deionized water (103 g), and 3% potassium persulfate aqueous solution (8.3 g) were added to the reactor, and the bottle was sealed and then evacuated. Butadiene (25 g) was charged into the reactor and the system was aged at 65°C for 24 h (yield = 98%). The yield was measured by gravimetry of the nonvolatile compounds. The obtained latex was kept for 4 h at 70°C under nitrogen bubbling to evaporate unreacted any butadi-

ene. The insoluble polymer part in toluene was 98%, which consists of PTFE and crosslinked PB.

Preparation of the Graft Polymer Particles

The graft polymer latexes were prepared by batch and semicontinuous emulsion polymerization. The reactor was 1-L separable flasks equipped with ports for nitrogen, a condenser, a dual four-bladed marine-type propeller, an alcohol thermometer, and monomer introduction. Thirty percent of the composite polymer latex as the seed (400 g), 30% potassium laurate (5.4 g), and deionized water (76 g) were charged to the reactor. The stirring was effected by the stirrer, with a downward flow at 100 rpm. 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 (26 g) and acrylonitrile (10 g), 57% DHP (0.71 g), and the reductant solution [iron(II) sulfate heptahydrate (12 mg), dextrose (0.75 g), sodium pyrophosphate (0.6 g), and deionized water (25 g)] were added. After 1 h, the monomer emulsifier with initiator [styrene (103 g), acrylonitrile (41 g), deionized water (118 g), 30% potassium laurate (11 g), and 57% DHP (0.36 g)] was continually added at a constant rate for 4 h using a syringe pump. Finally, 57% DHP (0.36 g) and the reductant solution [iron(II) sulfate heptahydrate (3 mg), dextrose (0.25 g), sodium pyrophosphate (0.2 g), and deionized water (8.3 g)] were added to the stirred solution, and the reaction was continued for 1 h (yield = 98%). The polymers were coagulated by pouring hot water, in which two parts of calcium chloride had been dissolved into this latex. After washing with water several times, the polymers were dried at 75°C for 12 h.

Grafting Efficiency, Graft ratio and Intrinsic Viscosity of Nongraft Copolymer

The grafting efficiency and the graft ratio of the polymer were determined by solvent extraction with acetone (a solvent for SAN but not for PB and PTFE). Acetone solutions of the dried polymer (5% by volume) were prepared in 2-oz bottles, which were capped and shaken for 6 h at room temperature; the solution were centrifuged at 30,000 in an Hitachi Model CR-26H Preparation Ultracentrifuge for 30 min at 0°C; then, the super-

Table I Effect of Crosslink Density of PB on the Morphology of Structured Latex Particle Consisting of PTFE/Core and PB/Shell^a

Sample	Addition of <i>tert</i> -Dodecanetriol (g)	Yield (%)	Composition PTFE/PB (wt %)	Insoluble Polymer Part (%)	Morphology		Secondary Particle of PB
					Type	Figure	
1	None	98	50/50	98	Core-shell	1-(a)	No
2	0.25	96	49/51	81	Core-shell	1-(b)	Yes
3	0.75	91	48/52	75	Core-shell	1-(c)	Yes

^a [PTFE]₀/[butadiene]₀ = 25g/25g.

nant layer were pouring into a tared aluminum pan and dried, first at 60°C and then 24 h at 90°C *in vacuo*: the sample was then cooled in a desicca-

tor for 6 h and weighed. The fraction of soluble SAN was determined from the percent solid corrected final percent conversion. The grafting effi-

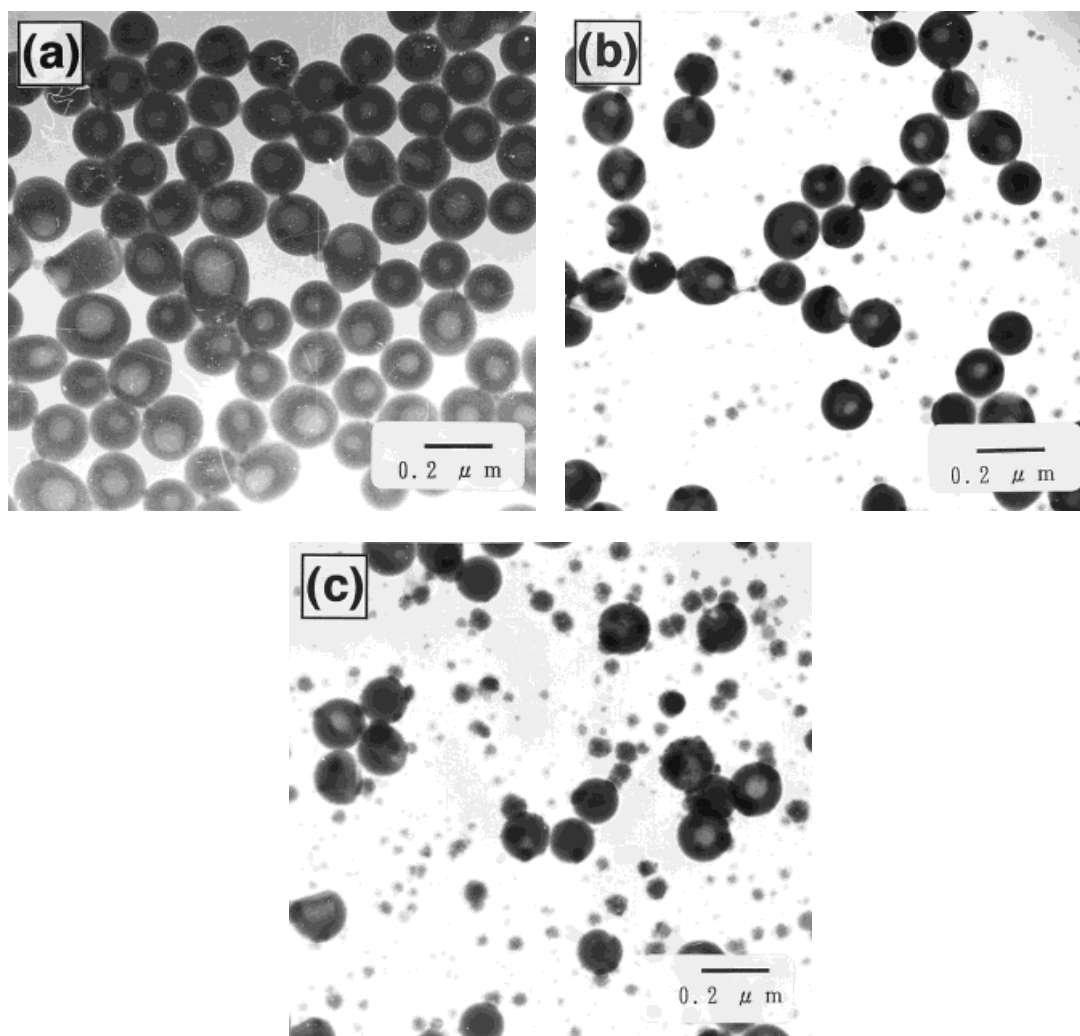


Figure 1 TEM of PTFE/PB core-shell composite particles (a) sample 1, Table I, (b) sample 2, Table I, and (c) sample 3, Table I.

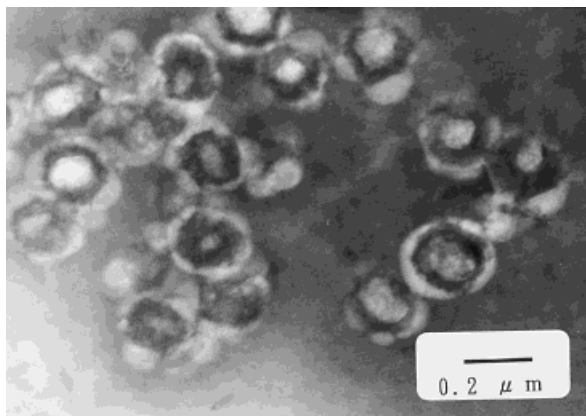


Figure 2 TEM of graft polymer particles protected by epoxy resin and stained by osmic acid [the seed composite particle: sample 1, Table I, Fig. 1(a)].

ciency and the graft ratio were calculated by the following equations:

grafting efficiency (%)

$$= \frac{\text{weight of grafted SAN}}{\text{total weight of polymerized SAN}} \times 100$$

graft ratio (%)

$$= \frac{\text{weight of grafted SAN}}{\text{weight of PTFE/PB core-shell particles}} \times 100$$

The fraction of soluble SAN: nongraft copolymer, having intrinsic viscosity of 0.5 g/L, measured at 30°C at 2-butanone. Replicate determinations were carried out for each latex recipe, and the grafting efficiency and the intrinsic viscosity were averaged.⁷

Contact Angle of Water Droplet

The polymer was coagulated by pouring the latex into acetone to remove the emulsifier, residual

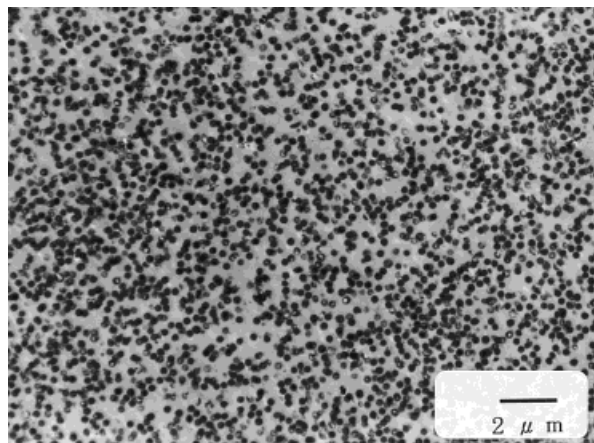


Figure 3 TEM of the blend the raw product of graft polymer particles with SAN stained by osmic acid [the seed composite particle: sample 1, Table I, Fig. 1(a)].

monomer and initiator (nongraft copolymer), and then dried *in vacuo* for 12 h. The contact angle of the water droplet of the polymer was measured using a the personal image analysis system (LA-252R/M8; Pias Co., Ltd.).

TEM Observation

The latex of composite particles was exposed to osmic acid vapor at room temperature for 30 min for definition, and was observed with the TEM. Graft polymer particles were surrounded by an epoxy resin, then stained by osmic acid. The blends prepared by mixing the raw product of graft polymer (40 wt %) with SAN (60 wt %) were molded with twin screw extruder at 230°C. The ultrathin cross section of the moulded sample was also stained by osmic acid, and was observed with TEM.

Table II Interface Free Energy of Polymer to Water

Sample	Contact Angle for Water θ	$\gamma_{\text{polymer-Air}}^a$ (10^{-3} J/m ²)	$\gamma_{\text{polymer-Water}}^b$ (10^{-3} J/m ²)	ΔG^c (10^{-3} J/m ²)
PTFE	119	4.83	40.1	0
PB	107	9.11	30.4	-9.7

^a $\gamma_{\text{polymer-Air}}$ was calculated according to the following equation: $\gamma_{\text{polymer-Air}} = \gamma_{\text{Water-Air}} (1 + \cos \theta)^2/4$, where $\gamma_{\text{polymer-Air}}$ and $\gamma_{\text{Water-Air}}$ are the surface free energies of polymer and water, respectively.

^b $\gamma_{\text{polymer-Water}}$ was calculated according to the following Young's equation: $\gamma_{\text{polymer-Water}} + \gamma_{\text{Water-Air}} \cos \theta = \gamma_{\text{polymer-Air}}$.

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

Table III Interface Free Energy of Polymer to Water^a

Sample	Contact Angle for Water θ	$\gamma_{\text{polymer-Air}}$ (10^{-3} J/m^2)	$\gamma_{\text{polymer-Water}}$ (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 as described in Table II.

RESULTS AND DISCUSSION

Effect of Crosslink Density of PB on the Morphology of Structured Latex Particle

The effects of the crosslink density of PB on the morphology of the structured latex particles were investigated. The results are summarized in Table I. The TEM of the latexes are shown in Figures 1–3. The white and black regions in the particles shows PTFE and PB, respectively. In all cases, the morphology of composite particle consists of a PTFE/PB core-shell structure. Based on the insolubility of the organic solvent in PTFE, the mechanism of core-shell particle formation should be considered. The growing PB chain produced in water might precipitate onto the surface of the PTFE particle and continue to propagate to form the shell layer. This mechanism may differ from that of the core-shell particles whose core was formed of crosslinked PDMS with shell composed of PB⁵ because the PDMS possesses high swelling ability for monomer.^{8–10} Phase separation between PTFE and PB in composite particles can be explained as follows: as summarized in Table II, this morphology is thermodynamically stable, because the free energy for forming the core-shell composite particles becomes very small.^{8,11} γ_{A-B} is the interface free energy of the two polymers *A* and *B*, while $\gamma_{C-Water}$ is the interface free energy of the initial latex particles against water. $\gamma_{B-Water}$ and $\gamma_{A-Water}$ are the interface free energy of polymer *A* against water and polymer *B* against water, respectively; there is no chemical bond be-

tween PTFE and PB because oxyradical could not the abstract fluorine atom of PTFE.^{12,13}

On the other hand, PB secondary particle formation significantly depended on the crosslink density of PB. The increase in crosslink density of PB resulted in depressing the formation of the PB secondary particles. The formation of PB secondary particles is considered as follows. The decrease in PB crosslink density results in increasing the aqueous-phase concentration of the PB radicals consisting of a 1–3 monomeric unit¹⁴ to promote aggregation to each other and to form the PB secondary particles.¹⁵

Graft Polymerization onto Composite Particles and Their Morphology

The drastic increase in grafting efficiency (0% → 70%) was able to be accomplished by the good coverage of the crosslinked PB shell on the PTFE particles. The graft ratio of the polymer and the intrinsic viscosity of the nongraft copolymer showed 103% and 0.944, respectively. TEM of the graft polymer particles is shown in Figure 2. The white regions around the particles show the graft layer of SAN. The thickness of the SAN's graft layer was about 0.03 μm . Therefore, each graft polymer particle independently exists without coalescence of the particles. This PTFE/core-PB/shell-SAN/shell morphology is thermodynamically stable because free energy for forming this structure becomes small as shown in Table III.

Table IV Contact Angle for Water

Sample	PTFE	Composite Particle	Graft Polymer ^a Particle
Contact angle for water θ	119	102	64

^a Graft copolymer was isolated with acetone.

Properties of the Composite Particles and the Graft Copolymer

The increasing adhesion with water was able to be carried out by good coverage of PB onto PTFE surface and by grafting of styrene and acrylonitrile onto the PB shell, as summarized in Table IV.

SAN-modified PTFE PB core-shell particles

could eventually be dispersed homogeneously in a SAN matrix, as shown in Figure 3.

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REFERENCES

1. G. Koo, in *Fluoropolymers*, L. A. Wall, Ed., Wiley-Interscience: New York, 1972.
2. T. Satokawa, *Fundamental Fluoropolymer*, Nikkan Kogyo Shinbunsha: Tokyo, 1982.
3. Y. Yamada, T. Yamada, S. Tasaka, and N. Inagaki, *Macromolecules*, **29**, 4331 (1996).
4. E. T. Kang, K. L. Tan, K. Kato, Y. Uyama, and Y. Ikada, *Macromolecules*, **29**, 6872 (1996).
5. M. Okaniwa and N. Kawahashi, *Colloid Polym. Sci.*, **275**, 315 (1997).
6. M. Okaniwa and Y. Ohata, *J. Polym. Sci., Polym. Chem. Ed.*, **35**, 2607 (1997).
7. E. S. Daniels, V. L. Dimonie, M. S. El-Aasser, and J. W. Vanderhoff, *J. Appl. Polym. Sci.*, **41**, 2463 (1990).
8. W. He, J. Tong, M. Wang, C. Pan, and Q. Zhu, *J. Appl. Polym. Sci.*, **55**, 667 (1995).
9. E. Favre, *Eur. Polym. J.*, **32**, 1183 (1996).
10. M. Okaniwa, *Polymer*, in press.
11. E. J. Sundberg and D. C. Sundberg, *J. Appl. Polym. Sci.*, **47**, 1277 (1993).
12. M. J. Cuthbertson, E. Rizzardo, and D. H. Solomon, *Aust. J. Chem.*, **38**, 315 (1985).
13. I. H. Elson, S. W. Mao, and J. K. Kochi, *J. Am. Chem. Soc.*, **97**, 335 (1975).
14. J. L. Ammerdorffer, A. A. G. Lemmens, A. L. German, and F. M. Everaerts, *Polym. Commun.*, **31**, 61 (1990).
15. W.-D. He, C.-T. Cao, and C.-Y. Pan, *J. Appl. Polym. Sci.*, **61**, 383 (1996).