

Composite Polymer Particles with a Graded Resin Composition by Suspension Polymerization

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ABSTRACT: We have conducted a study of composite polymer particles with a graded resin composition by suspension polymerization, in which the resin composition gradually changes from the surface to the center of the particles. The binder resin of the polymer particles consists primarily of styrene, butyl acrylate, and methacrylic acid (MAA). Fourier transform infrared/photoacoustic spectroscopy analysis of the polymer particles by suspension polymerization has proved that MAA, having a higher polarity, concentrates near the surface of the particles, and this results in a formation similar to a core-shell structure. These composite polymer particles are excellent in blocking resistivity

because the resin, containing a higher concentration of MAA, has a high glass-transition temperature. Composite polymer particles with a graded MAA concentration could be used for toner applications in low-power hot-roll fusing electrophotography systems because the melting property of the core resin is controlled and allows fusing at lower temperatures. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 682–690, 2005

Key words: composites; microencapsulation; particle size distribution; polystyrene

INTRODUCTION

In efforts to achieve increasingly high-resolution electrophotography images, the printing process and the materials involved in electrophotography are constantly being improved. Resolution enhancement requires toner particles with very small particle sizes over a narrow size range distribution. Toner particles are currently produced by a pulverization method. The production costs are disadvantageous if the particle size distribution is controlled and the particle size is reduced.

In contrast, the production of toner particles with the suspension polymerization method is attracting attention because it uses a simpler method for the synthesis of smaller toner particles with a narrower distribution.^{1,2} In addition to this, in suspension polymerization, polymer particles are directly formed by the polymerization of a monomer droplet in a water medium, and the binder resin properties can easily be controlled through variations of the monomers and polymerization.³

In hot-roll fusing systems, toner particles are generally fused to paper with pressure and thermal energy.

Because this thermal energy accounts for most of the electric energy consumed by electrophotographic printers and copiers, low-temperature fusibility has long been sought as a way of reducing energy costs and has become increasingly important for toner particle resins. Generally, a toner resin melts easily at low temperatures when its molecular weight is low or when its glass-transition temperature (T_g) is low. However, toner particles made of a resin with low-temperature melting points tend to block one another.

To achieve lower temperature fusing and eliminate blocking, the toner resin should be given both a lower softening temperature (T_s) and a higher T_g . However, lowering T_s of the resin lowers T_g . As a result, a toner particle with a low T_s value tends to cause blocking at lower temperatures. To reduce toner blocking, a core-shell structure with low T_s and T_g values at the core and a high- T_g layer at the surface has been suggested.⁴

The core-shell structure is typically formed by the interfacial reaction between reactants in the oil and water phases. However, this surface layer does not easily melt because of its high crosslink density, and while improving the blocking resistivity, it inhibits the fusibility of the toner.

In this study, for the purpose of improving the blocking resistivity without decreasing fusibility, the synthesis of toner particles with simpler suspension polymerization in the presence of a polar monomer

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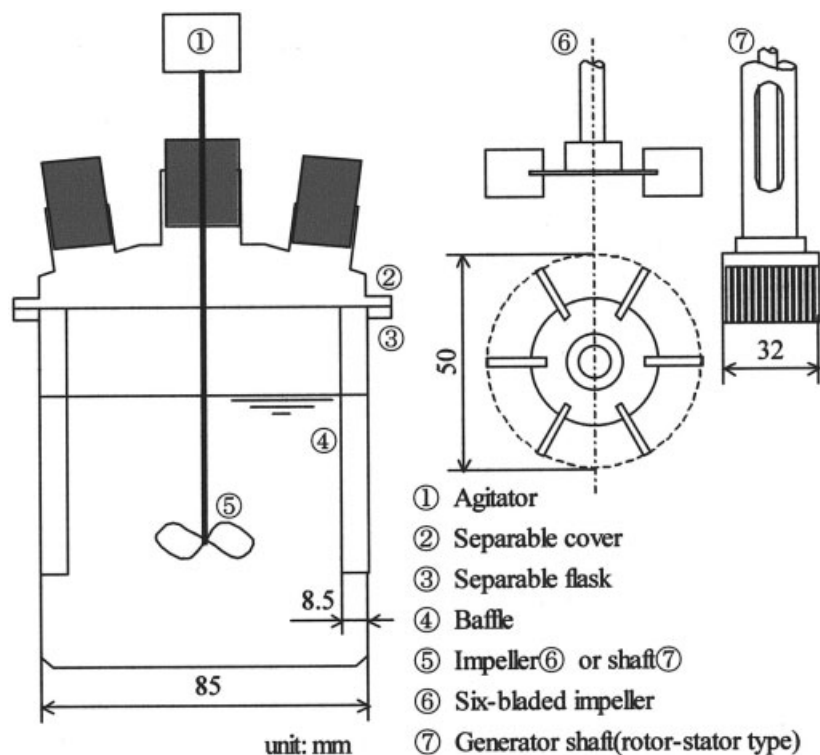


Figure 1 Experimental apparatus.

was investigated to form core-shell structured particles. In addition, Fourier transform infrared/photoacoustic spectroscopy (FTIR-PAS) analysis was carried out to evaluate how the resin composition changed from the surface to the center of the particles.

EXPERIMENTAL

Materials

Styrene (St), *n*-butyl acrylate (BA), divinyl benzene (DVB), and methacrylic acid (MAA) monomers were reagent-grade. St was washed with 0.1N sodium hydroxide to remove the polymerization inhibitor. The radical initiator for polymerization was 2,2'-azobis(2,4-dimethyl valeronitrile) (ADVN; V-65, Wako Pure Chemical Co., Osaka, Japan), and tricalcium phosphate (TCP; Wako Pure Chemical, Osaka, Japan) and sodium dodecyl benzene sulfonate (DBS; Wako Pure Chemical, Osaka, Japan) were used as the suspension stabilizer and costabilizer, respectively. The magnetic powder used to impart the magnetic property to the polymer particles was magnetite (BL-200, Titan Kogyo, Ube, Japan), and the particle size of the magnetite powder ranged from 0.1 to 0.25 μm in diameter. *N*-Decyltrimethoxysilane (DTMS; KBM3103, Shin-Etsu Chemical Co., Tokyo, Japan) as a treatment agent was used for the hydrophobic treatment of the magnetite powder surface.

Apparatus

Figure 1 shows the experimental apparatus used for preparing composite polymer particles. A separable flask, with an inner diameter of 8.5×10^{-2} m and a capacity of 5×10^{-4} m³, was used as the reactor. Four baffles, 8.5×10^{-3} m wide, were installed on the wall of the reactor to prevent air entrainment from the free surface of the dispersion with stirring. A high-speed mixer with a generator shaft (Phycostron, SMT Co., Tokyo, Japan) was used to form monomer droplets in the water continuous phase. The impeller of a six-bladed disk turbine, 5.0×10^{-2} m in diameter, was used as a stirrer during suspension polymerization and installed at half of the liquid depth.

Preparation of the polymer particles

The treatment of the magnetite powder surface by DTMS was carried out before suspension polymerization. A toluene solution of 0.10 mol/L of DTMS was prepared, and the magnetite powder was added to the solution, which was then stirred at a temperature of 110–120°C for 5 h. Thus, the magnetite powder was treated with DTMS. After this process, the magnetite powder was washed with methanol to remove the excess DTMS and dried at room temperature for a day after the filtering operation.

The preparation of the polymer particles was as follows. The dispersed phase was a monomer mixture

TABLE I
Monomer Formulation

No.	Monomer weight ratio (wt %)			
	St	BA	DVB	MAA
1	69.7	29.8	0.5	0
2	69	29.5	0.5	1
3	67.6	28.9	0.5	3
4	66.2	28.3	0.5	5

of St, BA, DVB, and MAA as a polar monomer in which 4 wt % monomer of ADVN and 40 wt % monomer of magnetite powder treated with DTMS were premixed for 5 min at a revolution speed of 100 s⁻¹ with a homogenizer (Masuda Rika Kogyo, Osaka, Japan). The monomer formation is shown in Table I.

The continuous phase was prepared by the dissolution of 2 wt % water of TCP and 100 ppm water of DBS in distilled water. The dispersed monomer phase was poured into the continuous water phase and stirred for 0.5 h at a revolution speed of 167 s⁻¹ with a high-speed mixer to form an oil-in-water dispersion. Then, suspension polymerization was carried out for 6 h at a polymerization temperature of 70°C in a nitrogen atmosphere and at an impeller speed of 3.3 s⁻¹. To remove TCP from the surface, 50 g of polymer particles was added to 500 mL of 0.1M hydrochloric acid, and the mixture was stirred for 0.5 h, filtered, and washed with an excess amount of water until the pH of the filtrate became neutral. Finally, the polymer particles were dried for a day *in vacuo* at room temperature.

Characterization

The surface morphology of the polymer particles was observed with scanning electron microscopy (SEM). The dispersion state of the magnetite powder in the particles was observed with transparent electric microscopy (TEM) at an intensity of 125 kV. The sample for TEM observation was an ultrathin film sliced with a glass knife equipped in a microtome.

The particle size distributions and mean diameters of the polymer particles were then measured with a Coulter Multisizer II particle size analyzer (Coulter Electronics, Inc., Luton, UK) after polymerization.

The resin composition of the particles was evaluated by FTIR-PAS with both a Fourier transform infrared spectrometer (FTS-60A/896, Bio-Rad Digilab, Hercules, CA) and a photoacoustic detector (model 200, MTEC Photoacoustics, Inc., Ames, IA).

FTIR-PAS has been proved to be an effective tool for both depth profiling analysis and the determination of the chemical group concentrations of polymer materials. Another advantage of this spectroscopy is that powdered samples such as toner particles are also

available for measurements. A depth profile can be obtained by changes in the scanning velocity of the mobile mirror. Spectra evaluated at a high scanning velocity show the area close to the surface, whereas those at a low scanning velocity show the deeper area. The scanning velocities of the mobile mirror in this measurement were in the range of 0.16 (2.5 kHz) to 1.28 cm/s (20 kHz). These mirror velocities correspond to modulation frequencies of 256–2048 Hz at 1600 cm⁻¹. The scanning number was between 64 and 256. The spectral resolution was set at 4 cm⁻¹. The measurement conditions are listed in Table II.

The T_g for each polymer particle was measured with a differential scanning calorimeter (DSC-910, DuPont, Wilmington, DE). The sample weight and the heating rate were 10 mg and 5°C min⁻¹, respectively. The sample was prepared via melt quenching at 170°C for 5 min before the differential scanning calorimetry measurement. T_s was measured with a flow tester (CFT-500, Shimadzu Co., Kyoto, Japan), which was a melt testing instrument for the measurement of the melt flow rate or melt volume rate. T_s was determined as the temperature for the plunger movement of 4 mm under 20 MPa of pressure and at a heating rate of 6°C min⁻¹. A die with an orifice 1 mm in diameter was used in this measurement.

The blocking ratio was obtained as follows. The polymer particles were heated in a plastic bottle at 45°C for 8 h, and then the content was sifted with a sieve. The blocking ratio was calculated from the ratio of the residue on the sieve to the total amount as follows:

$$\text{Blocking ratio(\%)} = \left(\frac{\text{Residue of particles}}{\text{Total amount of particles}} \right) \times 100 \quad (1)$$

The fusibility of the toner particles to paper was measured by a tape adhesion test, as shown in Figure 2. The adhesive tape (Scotch mending tape, Sumitomo 3M, Tokyo, Japan) was placed on fixed images printed with a Fujitsu Print Partner 8000 Luminous Electric Diode (LED) printer. A roll pressure of 6 MPa was placed on the adhesive tape, and the tape was removed at a speed of 1.0 cm/s. The fusibility was calculated from the optical density of the original image and remaining image as follows:

TABLE II
FTIR-PAS Measurement Conditions

Mirror velocity and scanning number	0.16 cm/s (2.5 kHz), 64
	0.32 cm/s (5 kHz), 64
	0.64 cm/s (10 kHz), 128
	1.28 cm/s (20 kHz), 256
Spectra resolution	4 cm ⁻¹

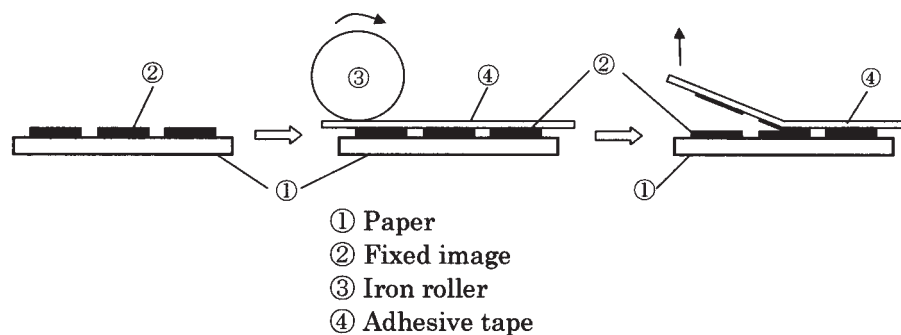


Figure 2 Tape adhesion test.

Fusibility(%)

$$= (\text{Remaining optical density} / \text{Original optical density}) \times 100 \quad (2)$$

The optical density of the image was measured with an optical densitometer (PDA-65, Konica Co., Tokyo, Japan).

RESULTS AND DISCUSSION

Morphology and particle size distribution

SEM photographs of the polymer particles with various concentrations of MAA and a TEM photograph of the polymer particle with 5 wt % MAA are shown in Figure 3. The surfaces of the particles are relatively smooth, and the particles without MAA and with MAA have many submicrometer-size (ca. 0.1–0.5 μm) byproduct particles on the surface. Magnetic powders are included well because of the hydrophobic property in the surface added by a treatment with a specific silane agent.

Figure 4 shows the particle size (d_p (μm)) distributions of the particles in various concentrations of MAA. The mean particle size (d_{p_a} (μm)) and particle size distribution of the particles are 7.5–9.5 μm and 37.2–41.6% according to coefficient of variance; standard deviation/mean diameter (CV), respectively. Differences in the mean particle sizes and particle size distributions can be observed for each particle; a higher MAA content resulted in a larger mean particle size and CV value. This result is considered to be attributable to the changes in the surface conditions of the particles: MAA concentrating near the surface of the particles acts to reduce the stabilization of the monomer droplets formed by the suspension stabilizer and costabilizer.

Resin composition

First, the relationship between the interferometer mirror velocity and the sampling depth of FTIR–PAS is

discussed. In this analytical technique, the IR radiation absorbed by the sample converts into heat within the sample. Subsequently, the heat diffuses to the sample surface and then into the surrounding gas atmosphere, thus causing gas expansion. The thermal expansion of the gas produces photoacoustic signals. The thermal diffusion length, μ (cm), which corresponds to the depth of heat diffusion that contributes to the temperature change on the surface of the sample, is defined as follows:⁵

$$\mu = \sqrt{\frac{k}{\pi f \rho c}} = \sqrt{\frac{D}{\pi f}} = \sqrt{\frac{D}{\pi \nu V}} \quad (3)$$

where k is the thermal conductivity ($\text{cal cm}^{-1} \text{s}^{-1} \text{ } ^\circ\text{C}^{-1}$), f is the modulation frequency (Hz), ρ is the density (g cm^{-3}), c is the specific heat ($\text{cal s}^{-1} \text{ } ^\circ\text{C}^{-1}$), and ν is the scanning velocity of the mobile mirror (cm s^{-1}). D is the thermal diffusivity ($\text{cm}^2 \text{s}^{-1}$); V is the volume (cm^3).

From eq. (3), it can be said that the thermal diffusion length, which is equivalent to the sampling depth of FTIR–PAS, is inversely promotional to the mirror velocity; in other words, a higher scanning velocity analyzes an area deeper from the sample surface.

The thermal diffusivity of the polymer particles used in the calculations is $0.6 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$; this assumes that the polymer contains 100% polystyrene.⁶ From eq. (3), the thermal diffusion lengths of the particles for each modulation frequency at 2048, 1024, 512, and 256 Hz have been calculated to be 3.0, 4.3, 6.0, and 8.7 μm , respectively. These data prove that this measurement covers an area 3 μm deep from the surface, nearly half the particle size and deep in the range of the whole particle.

Figure 5 shows the FTIR–PAS spectrum of a polymer particle without MAA measured at a mirror velocity of 0.16 cm/s; this measurement covers the area of the whole particle. The assignment of the main absorbance bands is also shown in Table III. The spectrum shows a strong peak at 1730 cm^{-1} corresponding to the C=O stretch bond of the ester group in BA and

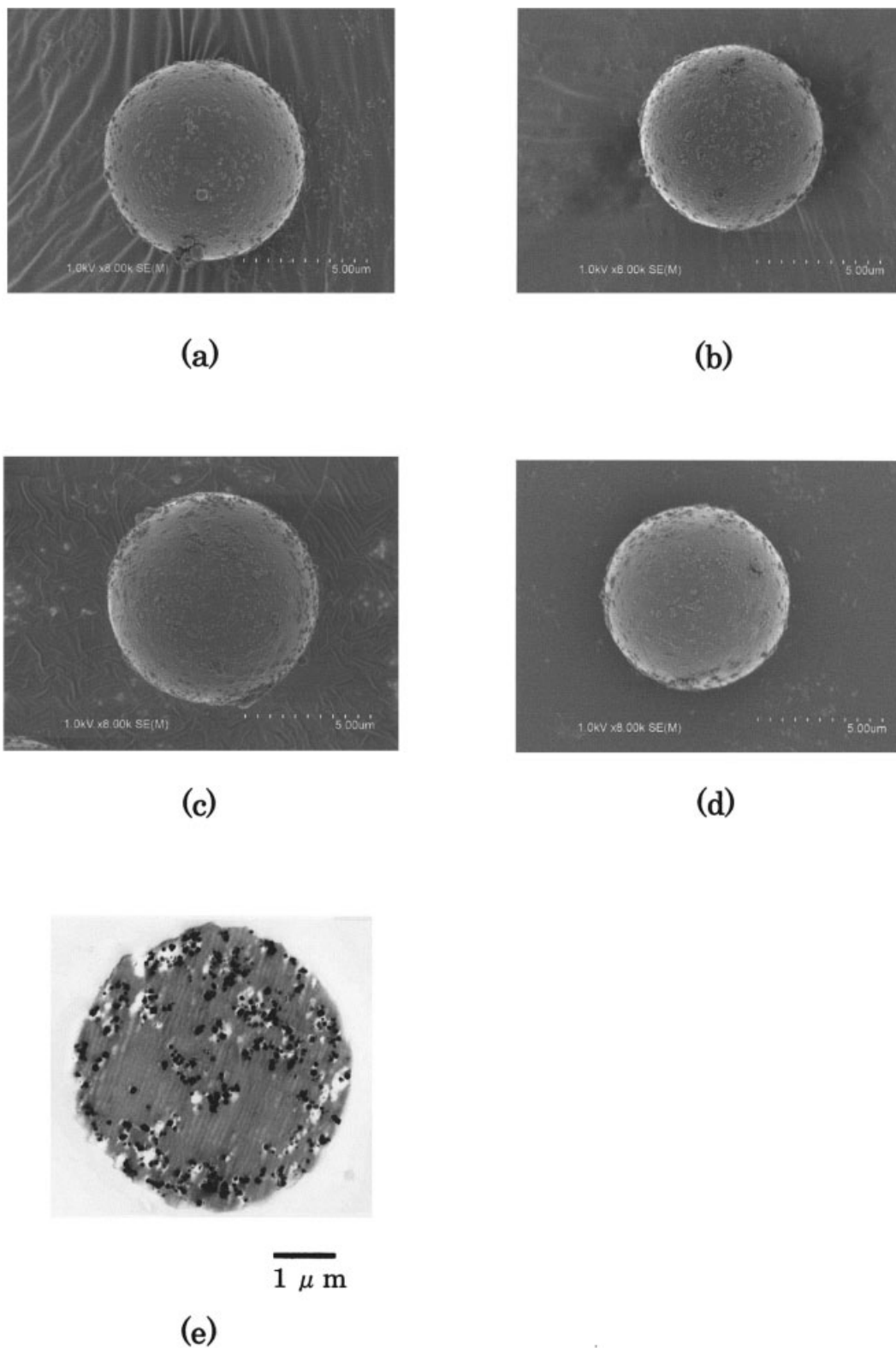


Figure 3 (a–d) SEM photographs of the polymer particles with 0, 1, 3, and 5 wt % MAA, respectively, and (e) TEM photograph of the polymer particles with 5 wt % MAA.

weak peaks at 1602 and 1493 cm^{-1} corresponding to the $\text{C}=\text{C}$ double bond of the phenyl group in St.

Figures 6–8 show the FTIR–PAS spectra of the wave-number range from 1800 to 1500 cm^{-1} of the

polymer particles with 1, 3, and 5 wt % MAA. All the spectra have a strong peak at 1730 cm^{-1} corresponding to the $\text{C}=\text{O}$ stretch bond of the ester group in BA, a weak peak at 1602 cm^{-1} corresponding to the $\text{C}=\text{C}$

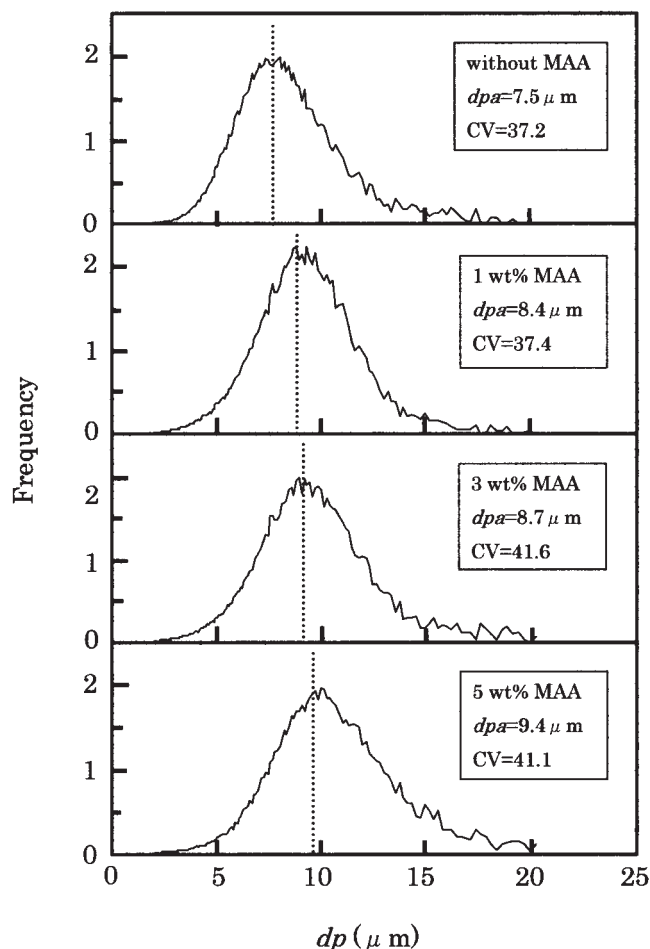


Figure 4 Particle size distributions of the particles with various concentrations of MAA.

double bond of the phenyl group in St, and a small peak at 1703 cm^{-1} corresponding to the C=O stretch bond of the carboxyl group, which verifies the existence of MAA. For a polymer particle with 5 wt % MAA, the peak of COOH in scanning at 1.28 cm/s is

TABLE III
Assignment of Main Absorbance Bands

Wave number (cm^{-1})	Assignment
2957	CH stretching ($-\text{CH}_3$)
2928	CH stretching ($-\text{CH}_2-$)
1730	C=O stretching ($-\text{COOR}$)
1602, 1493	In-plane skeletal (benzene ring)
1453	CH deformation ($-\text{CH}_3$, $-\text{CH}_2-$)
1372	CH deformation ($-\text{CH}_2-$)
1255, 1163	C—O—C stretching ($-\text{COOR}$)
1067, 1028	CH in-plane deformation (benzene ring)
760, 700	CH out-of-plane deformation (benzene ring)

stronger than that below 0.64 cm/s . This suggests that the concentration of MAA is higher in the surface of the polymer particles.

To evaluate the amounts of MAA and BA with respect to St at different depths of the polymer particles in various concentrations of MAA, the intensity ratios of the absorptions at 1703 and 1730 cm^{-1} to the absorption at 1602 cm^{-1} attributed to the phenyl groups in St have been calculated as follows:

$$\text{Intensity ratio} = I_{1703}/I_{1602}, \quad I_{1730}/I_{1602} \quad (4)$$

where I_{1703} , I_{1730} , and I_{1602} are the absorption intensities at 1703 , 1730 , and 1602 cm^{-1} , respectively.

Table IV shows the intensity ratios of peaks at 1703 and 1602 cm^{-1} and at 1730 and 1602 cm^{-1} . I_{1703}/I_{1602} is very small because of the low MAA level, but it increases when the MAA content is increased, especially when the mirror velocity is 1.28 cm/s , which covers the measurement near the surface. As evidence, relatively large intensity ratios can be seen with both 3 and 5% MAA. From these data, it can be said that the MAA concentration is higher at the surface of the polymer particles, and a graded resin composition is formed from the surface to the center. For BA, $I_{1730}/$

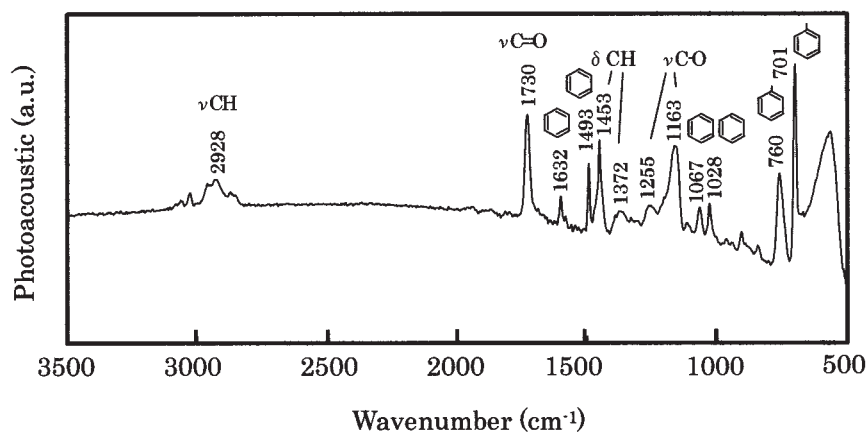


Figure 5 FTIR-PAS spectrum of a polymer particle without MAA measured at mirror velocity of 0.16 cm/s .

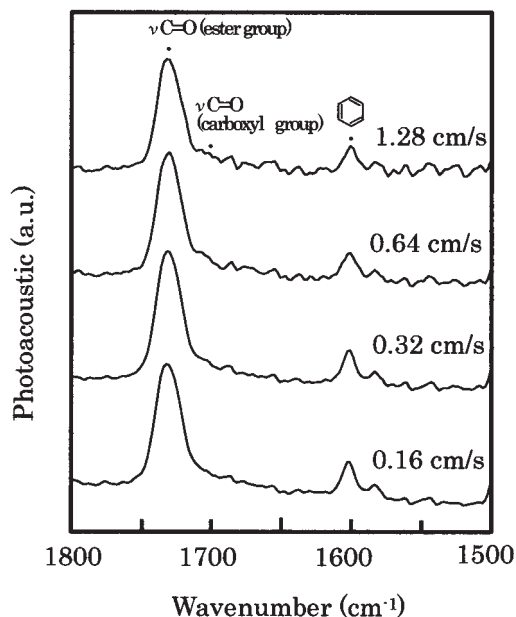


Figure 6 FTIR-PAS spectrum of a polymer particle with 1 wt % MAA.

I_{1602} at higher mirror velocities is also slightly larger. Figure 9 shows the process used to form the graded resin composition particles. The difference of affinity among the added monomers forms the gradation in the particles dispersed in the water medium. A polar monomer has a polar group, such as the carboxyl group in the MAA molecule, and shows an affinity to water. Thus, an arbitrary amount of MAA is soluble in water. BA has a slight solubility, and St is sparingly

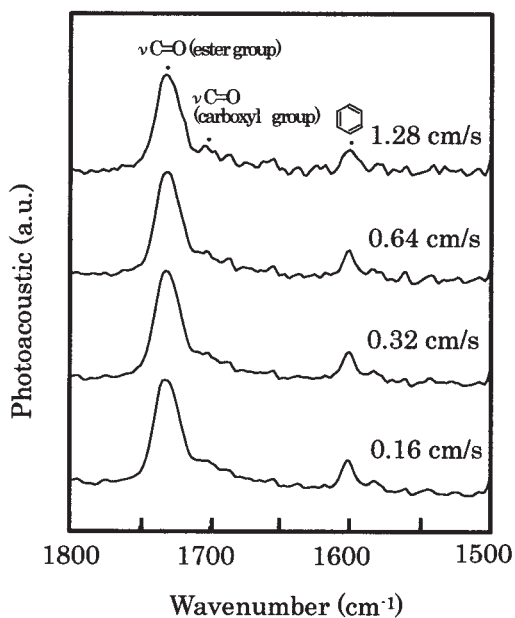


Figure 7 FTIR-PAS spectrum of a polymer particle with 3 wt % MAA.

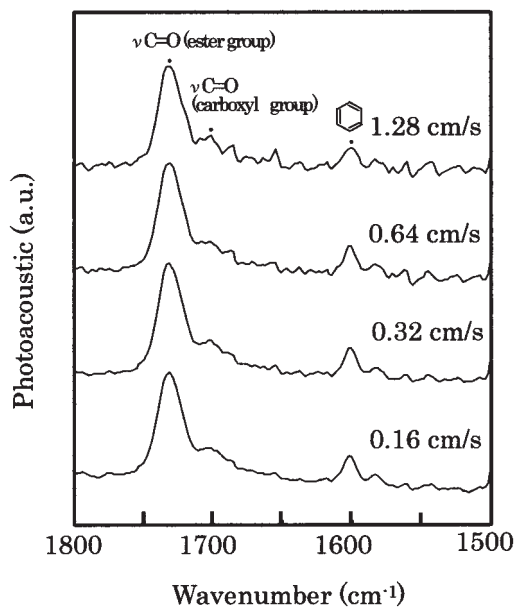


Figure 8 FTIR-PAS spectrum of a polymer particle with 5 wt % MAA.

soluble. Because MAA has the highest affinity for water in these three monomers, MAA tends to localize at the interface between the monomer and water that is equivalent to the surface of the particle. BA has a slight affinity for water, so gradation for BA is a little different.

Blocking resistively and fusibility

Table V and Figure 10 show the thermal properties and blocking resistivity of particles polymerized in

TABLE IV
Intensity Ratio of Carboxyl Groups and Ester Groups to Phenyl Groups in FTIR-PAS Spectra

MAA content (%)	Mirror velocity (cm/s)	Intensity ratio	
		I_{1703}/I_{1602}	I_{1730}/I_{1602}
0	0.16	—	3.92
	0.32	—	4.18
	0.64	—	4.07
	1.28	—	4.20
1	0.16	0.07	4.00
	0.32	0.08	4.38
	0.64	0.14	5.12
	1.28	0.16	4.52
3	0.16	0.17	3.93
	0.32	0.14	4.43
	0.64	0.24	4.15
	1.28	0.40	4.23
5	0.16	0.37	4.16
	0.32	0.40	4.13
	0.64	0.34	3.95
	1.28	0.73	4.92

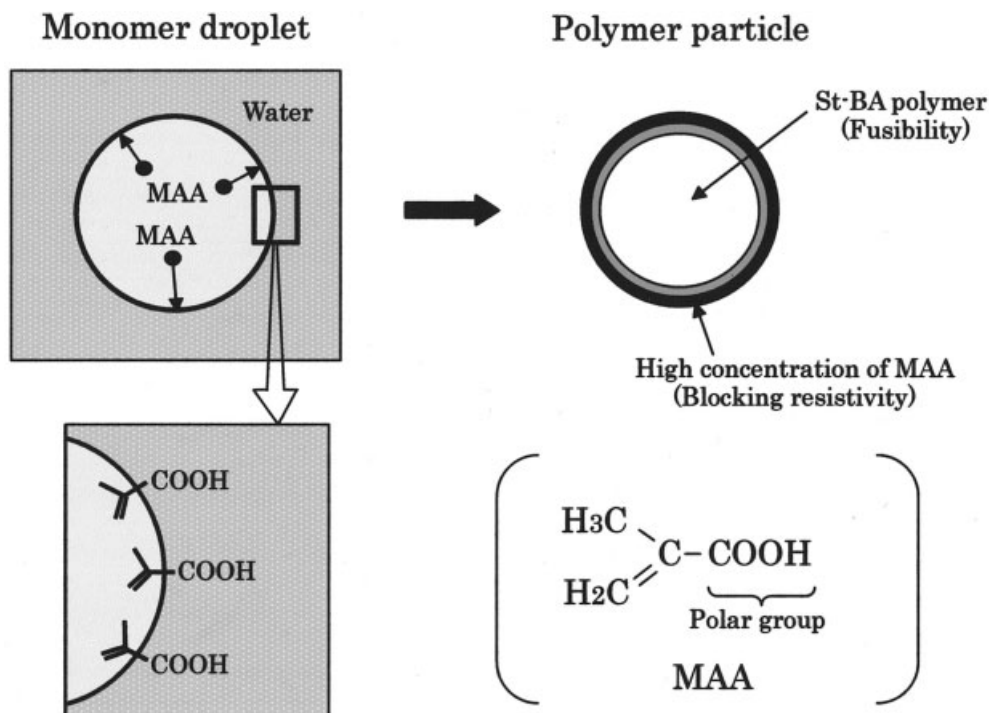


Figure 9 Schematic diagram of a polymer particle.

various concentrations of MAA. Both T_g and T_s of the particles are independent of any additions of MAA. In contrast, the blocking ratio of the particles is drastically reduced as the concentration of MAA increases. The T_g values of each homopolymer of St, BA, and MAA are 100, -54 , and 228°C , respectively.^{7,8} As a result, T_g of the resin rises as the concentration of MAA increases.

If the particle had a uniform resin composition, T_g of the particle would theoretically rise about 10°C for each addition of 5 wt % MAA, and blocking would be reduced more gradually. Therefore, it is thought that most of each particle is composed of St/BA resin, and only a small portion near the surface is composed of MAA and St/BA. This theory is supported by the results of FTIR-PAS analysis. The addition of MAA does not affect the thermal properties of the particles but does effectively reduce blocking between particles.

Figure 11 charts the fusibility of toner made with various amounts of MAA. Similar to the thermal prop-

erties, the fusibility of the toner particle does not seem to be affected by additions of MAA. The St/BA resin, which makes up most of the particle, is the predominant factor in toner fusibility. Therefore, blocking resistivity and fusibility can be individually controlled by variations in the properties of the surface resin and core resin. The former is successfully controlled by the concentration of MAA, and the latter is controlled by the St/BA ratio, molecular weight, and so on.

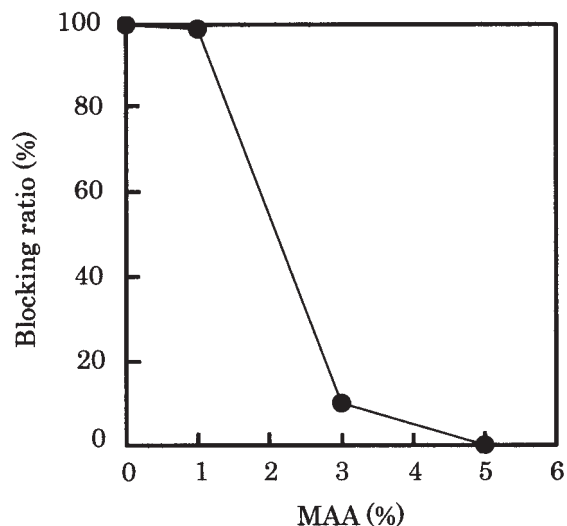


Figure 10 Relationship between the blocking ratio and the concentration of MAA under 45°C .

TABLE V
Thermal Properties of Polymer Particles Formed with the Addition of Various Amounts of MAA

MAA (%)	T_g ($^\circ\text{C}$)	T_s ($^\circ\text{C}$)
0	54	117
1	52	123
3	53	119
5	55	124

Figure 12 shows that the relationship between the blocking ratio and T_g . T_g of the core resin varies from 30 to 60°C for polymerizing monomer mixtures containing various ratios of St to BA and with other polymerizing conditions varied. The blocking ratio changes abruptly at 60°C without MAA and at 43°C with the addition of 5 wt % MAA. If the difference in the blocking temperature of 17°C between these two types of particles is caused by the difference in T_g of the toner surface, the concentration of MAA in the surface resin is not 5 wt % but is equal to 10 wt %.

Restricting MAA to the surface can achieve a low T_g value for the core resin and facilitate fusing at lower temperatures.

CONCLUSIONS

The synthesis of polymer particles by suspension polymerization in the presence of a polar monomer such as MAA has been investigated. FTIR-PAS analysis has been carried out to evaluate how the resin composition changes from the surface to the center of the particles. The following results have been obtained.

1. FTIR-PAS analysis for the polymer particles by suspension polymerization has proved that the concentration of MAA is higher at the surface of

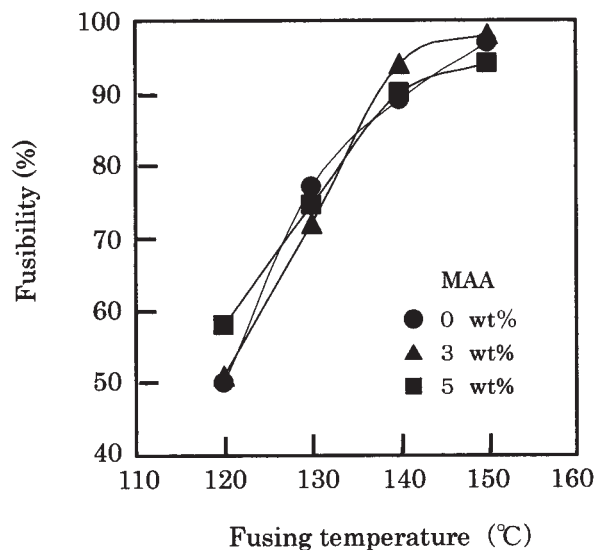


Figure 11 Fusibility at various hot-roll temperatures.

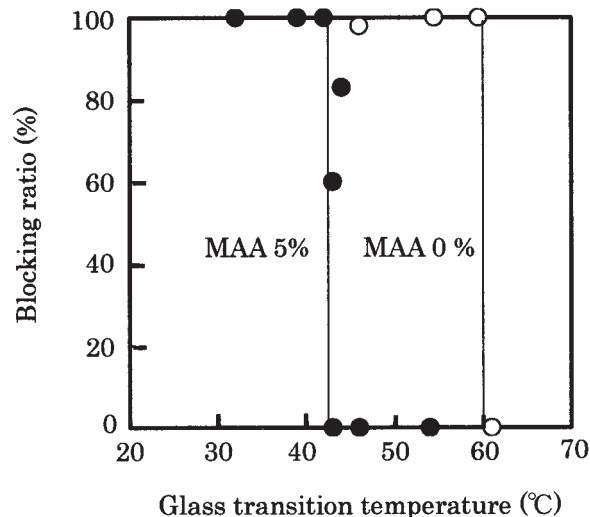


Figure 12 Relationship between the blocking resistivity under 45°C and T_g of the polymer particles.

the polymer particles, and this results in a formation like a core-shell structure.

2. The blocking resistivity is improved by the addition of MAA without a reduction of fusibility because the surface resin containing MAA has a higher T_g even if the core resin has a lower one.
3. Because the melt property of the core resin is controlled for fusing at lower temperatures, polymer particles with gradated MAA concentrations can be applied to toner applications for low-power hot-roll electrophotography fusing systems.

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