Toner with Gradated Resin Composition Made by Suspension Polymerization Technique

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Abstract

We have studied suspension polymerized toner with a gradated resin composition, in which the resin composition gradually changes from the surface to the center of the toner particle.

The binder resin of the toner consists of styrene, butyl acrylate, and methacrylic acid (MAA). In the suspension polymerization, MAA, having a higher polarity, concentrates near the surface of the toner. This toner is excellent in blocking resistivity, because the resin containing the higher concentration of MAA has a high glass transition temperature. Toner with a gradated MAA concentration can be used in low-power hot-roll fusing systems, if the melting property of the core resin is controlled for fusing at lower temperatures.

Introduction

To achieve high-resolution images in electrophotography, the printing process and the materials involved in electrophotography are constantly being improved. Resolution enhancement requires that toner have a very small particle size within a narrow size distribution.

Toner particles are currently produced by a pulverization method. The production costs are disadvantageous if particle size distribution is controlled and the particle size reduced. In contrast, production of toner using a polymerization method is attracting attention because suspension polymerization is a simpler method for synthesis of smaller toner particles having a narrower distribution.

In the suspension polymerization method, polymer particles are directly formed by the polymerization of a monomer droplet in a water medium. The properties of the binder resin can easily be controlled by varying the monomers and polymerization. The thermal properties of resin are very important factors for hot-roll fusing. Generally, the toner resin melts easily at low temperatures when its molecular weight is small and/or when its glass transition temperature is low. However, toner particles made of resin that melts at low temperatures tends to block each other.

In this paper, we will report on the synthesis of toner by suspension polymerization in the presence of a polar monomer for the purpose of improving blocking resistivity without decreasing fusibility.

Experiment

Suspension Polymerization

A monomer mixture of [Styrene (St): 69.7wt%, n-butyl acrylate (BA): 29.8wt%, divinyl benzene (DVB): 0.5wt%], methacrylic acid (MAA), magnetite powder treated with a coupling agent, and 2,2'-azobis(2,4-dimethylvaleronitorile) as an initiator were mixed with a high-speed mixer. This monomer mixture was added to a water medium containing tricalcium phosphate and sodium n-dodecylbenzenesulfonate as a suspension stabilizer. The mixture was then homogenized by a mechanical homogenizer. This suspension was polymerized at 70°C for six hours by agitation with a paddle. After polymerization, the suspension stabilizer was removed by acid. The polymerized particles were filtered out, rinsed with water, and dried.

Measurement

The gradated resin composition of the particles was evaluated by infrared spectroscopy using a photoacoustic cell (FT-IR/PAS). A depth profile was obtained by changing the scanning speed of a mobile mirror. The spectra evaluated at a scanning speed of 8mm/s show the area close to the surface, those at a scanning of 4mm/s show the deeper area. The blocking ratio was obtained as follows. Toner was heated in a plastic bottle at 45°C for eight hours. 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. The toner was blended with a carrier and used on an LED printer (Fujitsu Printpartner 8000). Fusibility was measured by the peel test on a solid square.

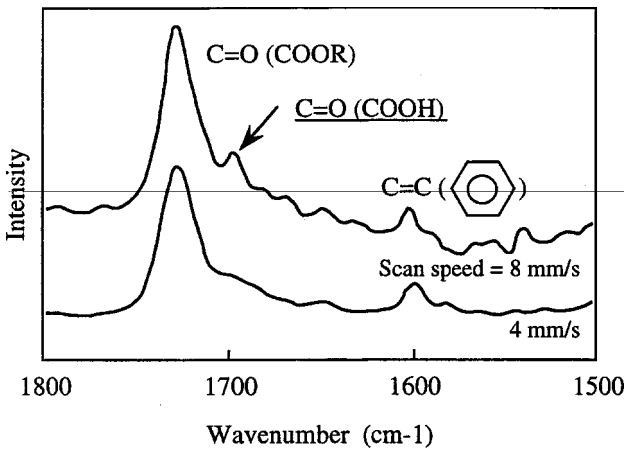

Figure 1. FT-IR/PAS spectra of toner polymerized in 5 wt% of MAA.

Results and Discussion

Resin Composition

Figures 1 and 2 show the FT-IR/PAS spectra of the polymerized toner with 5 wt% MAA and without MAA.

All the spectra have a strong peak at 1730 cm^{-1} and a weak peak at 1600cm^{-1}. The first peak shows the C = O stretch bond of the ester group in BA, the other shows the C = C double bond of the phenyl group in St. The spectra of the toner containing MAA have a small peak at 1700cm^{-1}, corresponding to the C = O bond of the carboxyl group, and exhibit the existence of MAA. The peak of COOH in scanning at 8mm/s is stronger than that at 4 mm/s, showing that the concentration of MAA is higher in the surface of the toner particle.

Table 1 shows the intensity ratio of C = O in the ester group (COOR) and C = O in the carboxyl group (COOH) to C = C in the phenyl group. At 8 mm/s, the COOH/C = C ratio is about four times that of 4 mm/s and a steep gradation of composition was formed from the surface to the center. At 8 mm/s, the COOR/C = C ratio is also slightly larger in spite of the presence of MAA.

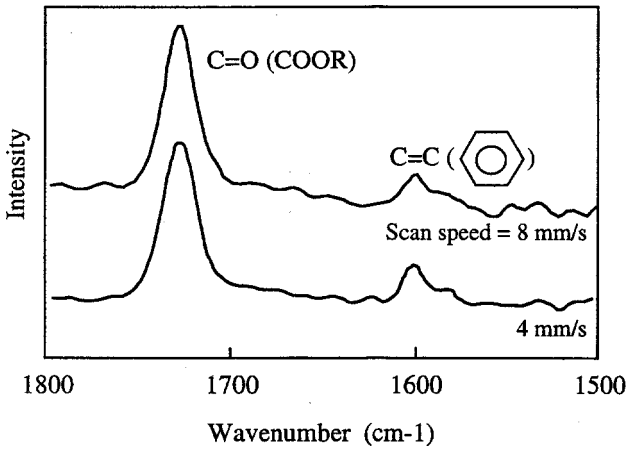

Figure 2. FT-IR/PAS spectra of toner polymerized without MAA.

Table 1. Intensity ratio of carboxyl group and ester group to phenyl group in FT-IR/PAS sepctra

MAA (wt%)	Scan speed (mm/s)	Intensity ratio COOH/C = C	COOR/C = C
5	8	0.9	7.1
	4	0.2	5.2
0	8	—	5.2
	4	—	4.0

Figure 3 shows the process used to form the gradated 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 solubility of 0.14g/100ml and St is sparingly soluble.[1] Because MAA has the highest affinity for water in these three monomers, MAA tends to localize at the interface between monomer and water that is equivalent to the surface of the toner particle. BA has a slight affinity for water, so that gradation for BA is a little different.

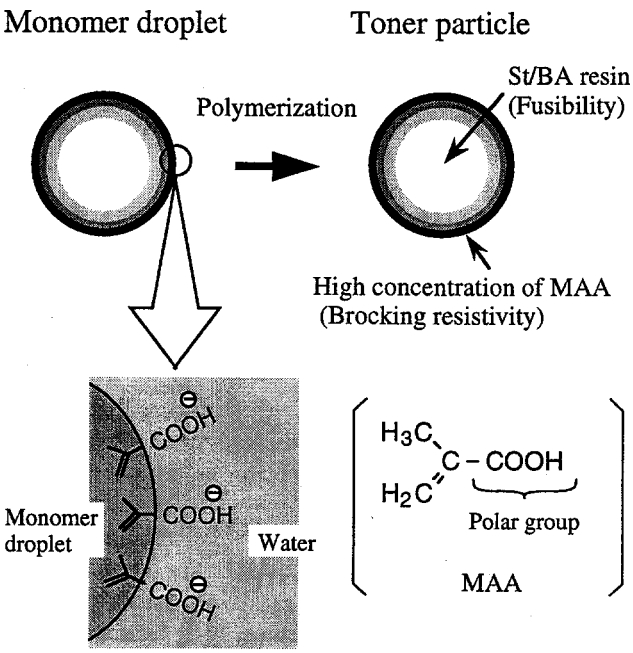

Figure 3. Schematic diagram of toner particle.

Blocking Resistance and Fusibility

Table 2 and Figure 4 show the thermal properties and blocking resistance of toners polymerized in various concentrations of MAA. Both the glass transition temperature and the softening temperature of the toner are independent of any additions of MAA. In contrast, the blocking ratio of the toner is drastically reduced as the concentration of MAA increases. The glass transition temperatures of each homopolymer of St, BA, and MAA are 100°C, -54°C, and 228°C,[2,3] respectively. As a result, the glass transition temperature of the resin raises as the concentration of MAA increases. If the particle had uniform resin composition, the glass transition temperature of the toner would theoretically rise about 10°C for each addition of 5wt% of MAA, and blocking would be reduced more gradually. Therefore, it is considered that most of a toner 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 FT-IR/PAS spectra analysis. The addition of MAA does not affect the thermal properties of the toner particles but does effectively reduce blocking between toner particles.

Table 2. Thermal properties of toner formed in various concentrations of MAA

MAA (wt%)	St/BA/DVB (wt%)	Tg (°C)	Tm (°C)
0	100	54	117
1	99	52	123
2	98	53	121
3	97	53	119
5	95	55	124

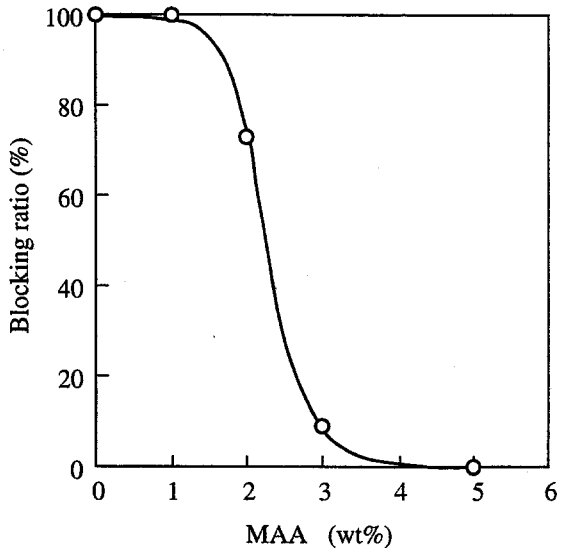

Figure 4. Relationship between blocking ratio under 45°C and concentration of MAA.

Figure 5 charts the fusibility of toner made with varying amounts of MAA. Similar to the thermal properties, the fusibility of the toner does not seem to be affected by additions of MAA. The St/BA resin, which makes up most of the toner, is the predominant factor in toner fusibility. Therefore, blocking resistivity and fusibility can be individually controlled by varying the properties of the surface resin and core resin. The former is successfully controlled by the concentration of MAA, the latter is controlled by the St:BA ratio, molecular weight, and so on.

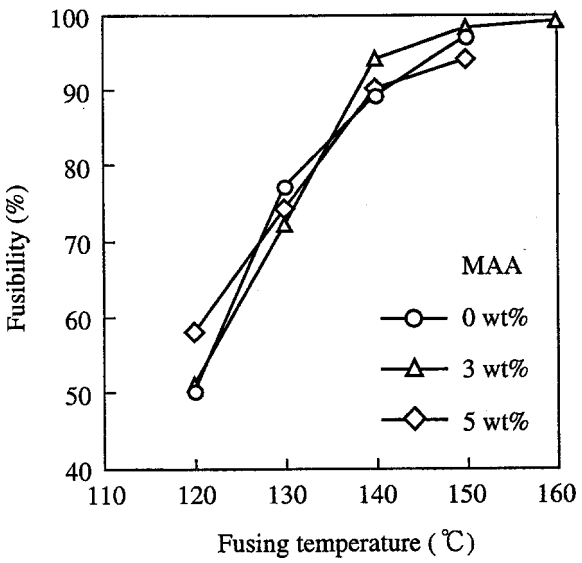

Figure 5. Fusibility at various hot-roll temperatures.

Figure 6 shows the relationship between the blocking ratio and the glass transition temperature. Glass transition temperatures of core resin were varied from 30°C to 60°C for polymerizing monomer mixtures containing various ratios of St to BA and by varying other polymerizing conditions. The blocking ratio changes abruptly at 60°C without MAA and at 43°C with the addition of 5 wt% of MAA. If the difference in blocking temperature of 17°C between these two types of toners is caused by the difference of the glass transition temperature of the toner surface, the contents of MAA in surface resin is not 5 wt% but equal to 10 wt%.

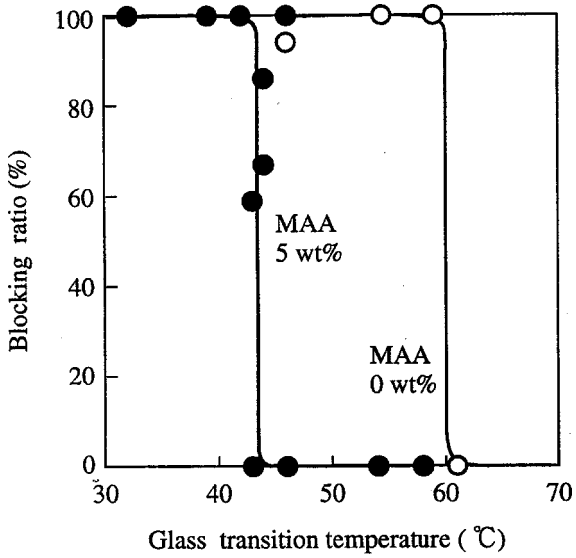

Figure 6. Relationships between blocking resistivity under 45°C and glass transition temperature to toner.

Restricting MAA to the surface can achieve a low glass transition temperature for the core resin and facilitate fusing at lower temperatures.

Conclusions

In the suspension polymerization of a toner composition containing a polar monomer such as MAA, the concentration of MAA is found to be higher at the surface of the toner particle.

Blocking resistance is improved by the addition of MAA without decreasing in fusibility, because the surface resin containing MAA has higher glass transition temperature even if the core resin has lower one.

If the melt property of the core resin is controlled for fusing at lower temperatures, the toner with gradated MAA concentrations can be applied to low-power hot-roll fusing systems.

References

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2. L. J. Hughes, G. L. Brown, *J. Appl. Polym. Sci.*, **5**, 580 (1961).
3. I. N. Razinskaya, N. E. Kharitonova, B. P. Shtarkman, *Vysokomol Soedin B*, **11**, 892 (1969).