Charge controlling capability of ultra-thin shell layers formed on a spherical PMMA core particle surface

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Abstract

Core-shell (C-S) particles having ultra-thin shell layers on the core particle surface are prepared with the coacervation process and their surface structure or tribo-charging characteristics are investigated. Spherical, positively chargeable polymethyl- methacrylate (PMMA) particles having a particle size of approximately 10 µm are used as the core particles. Negatively or positively chargeable ultra-fine particles having a particle size of 3 to 100 nm are used as the shell particles. Through the coacervation process in water, the shell particles are precipitated onto the core particle surface to yield C-S particles. From SEM observation and the blow-off tribo-charge measurements of the C-S particles, it is confirmed that (1) an ultra-thin single shell layer having a thickness of less than 20 nm and completely covering the underlying core surface is obtained, (2) the charging characteristics of the C-S particles are governed by the composition of the ultra-thin layer, (3) double shell C-S particles, in which a second ultra-thin shell layer is coated over the single shell C-S particles, are also obtained, (4) the charging characteristics of the double shell C-S particles are governed by the composition of the second ultra-thin shell layer.

Introduction

It is said that high quality core-shell (C-S) type toner can be obtained more easily in chemical toner than in pulverized toner. The remarkable feature of the C-S type toner is that it realizes toner in which several important functions required for the toner are shared among the core part and the shell part. The functions such as fluidity, tribo-charging, high durability, anti-coherent and anti-blocking properties, etc., are imposed on the shell part.1)

In our previous paper, the charge impartation capability of CCA particles that form a shell layer on a C-S particle surface was studied.2) An interesting result was obtained that the shell layer containing the CCA particles determines the charge impartation capability of the C-S particles. The result suggests that the CCA particles existing on the shell surface can be regarded as the most effective charge imparting particles for the tribo-charging of the C-S particles.

In this paper, negatively and positively chargeable ultra-fine copolymer shell particles having a particle size of 3 to 100 nm were used to build the shell layers. It was confirmed that the ultra-thin shell layers having a thickness of less than 20 nm completely cover the underlining core particle surface, and serve as accurate charge controlling shell layers. By selecting the shell particles, the polarity and the amount of charge are accurately controlled. Detailed results are mentioned below.

Experimental

Component materials for C-S particles

As core particles, positively chargeable spherical mono-disperse (PMMA) particles (Pc, diameter: 10µm) were used. As shell particles, negatively chargeable styrene-acrylic-acid copolymer particles (N, diameter: < 3 nm), positively chargeable trianilino-triphenyl methane sulfate particles (P_1, diameter: < 100 nm), and positively chargeable styrene-maleic-acid copolymer particles (P_2, cationically modified, diameter: < 3 nm) were used. The chemical structure of N, P_1 and P_2 particles are given in Fig. 1. These particles were dispersed in water, and the pH of the dispersion was adjusted to a prescribed value.

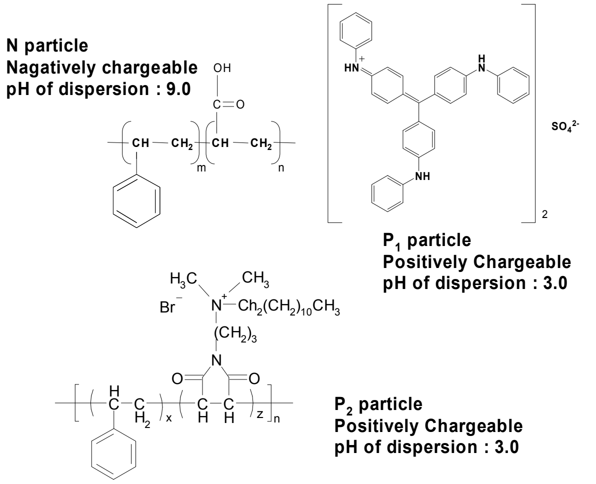

Fig.1 Chemical structure for three types of shell particles

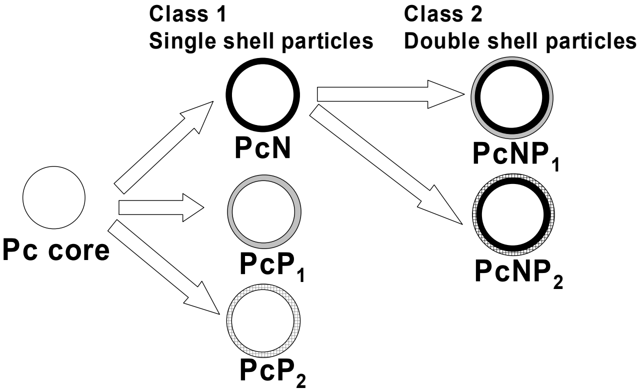

Fig.2 Structure of C-S particles prepar

C-S particles

Fig. 2 shows the structure of two classes of C-S particles prepared for this experiment. Class 1 consists of three types of single shell particles, PcN, PcP_1 and PcP_2, in which N, P_1 or P_2 particles form a single shell layer on the Pc core surface respectively. Class 2 consists of two types of double shell particles, PcNP_1 and PcNP_2, in which P_1 or P_2 particles form an upper shell on the PcN single shell C-S particle surface, respectively.

Table 1 shows the names and compositions of C-S particles of various types. The shell names consist of shell structure and shell composition. As for the particle name PcN 50, for example, PcN stands for the structure of single shell C-S particles (see Fig.2), and the figure 50 shows, in term of ppm, the amount of N particles that form the shell layer on the Pc core surface. Here, 1 ppm of shell particles corresponds to 10^{-4} wt% of particles per unit weight of core particles. For the preparation of the double shell C-S particles, PcN 5k single shell C-S particles were used as the core particles.

Table 1 Name and composition of C-S particles prepared

Class 1. Single shell particles

Type	Core particles	Shell particles	Particle names and compositions
P_CN	P_C	N	P_CN 50, P_CN 200, P_CN 1K, P_CN 5k, P_CN 20k
P_CP_1	P_C	P_1	P_CP_1 50, P_CP_1 200, P_CP_1 1K, P_CP_1 5k, P_CP_1 20k
P_CP_2	P_C	P_2	P_CP_2 50, P_CP_2 200, P_CP_2 1K, P_CP_2 5k, P_CP_2 20k

Class 2. Double shell particles

Type	Core particles	Shell particles	Particle names and compositions
P_CNP_1	P_CN 5k	P_1	P_CNP_1 50, P_CNP_1 200, P_CNP_1 1K, P_CNP_1 5k, P_CNP_1 20k
P_CNP_2	P_CN 5k	P_2	P_CNP_2 50, P_CNP_2 200, P_CNP_2 1K, P_CNP_2 5k, P_CNP_2 20k

The symbol "1 Kppm" means 1,000ppm.

Process for C-S particle preparation

As a typical example, a process for preparing PcN single shell C-S particles is mentioned below. A batch of 10 g of Pc core particles was mixed with 20 g of de-ionized water (DIW) containing 15 mg of sodium dodecylbenzensulfonate. Further, 170 g of DIW was added to the mixture. The temperature of the mixture was adjusted to 50ºC. The mixture was agitated vigorously, and a prescribed amount of N particle dispersion was added. Then, 0.1 N hydrochloric acid was added dropwise to adjust the pH of the mixture to 4.0. Mixing was continued for 30 min to form the N particle shell layer on the Pc core surface. The mixture was then cooled to room temperature to obtain the PcN single shell C-S particles. The resultant particles were washed with DIW by means of decantation. A wet cake of the PcN particles was obtained through filtration. The cake was left at 50ºC for 24 h to obtain a dried PcN particle sample.

SEM observation

The surfaces of all C-S particle samples in Table 1 were investigated by SEM observation.

Tribo-charge measurement

The amount of tribo-charge *q/m* was measured by the blow-off method complying with the standard measurement procedure stipulated by ISJ.[3)]

Results and Discussion

SEM observation of C-S particles

From the SEM observation, it was confirmed that the surface smoothness of the C-S particles was affected by the amount of shell particles which formed the shell layer on the C-S particle surface, and by the size of the shell particles. All the PcN, PcP_1 and PcP_2 single shell C-S particle surfaces that were formed from 50, 200, 1k and 5 kppm of N, P_1 and P_2 shell particles, respectively, were maintaining almost the same smoothness as that seen on the Pc core particle surface.

Fig. 3 shows the selected SEM photographs of three types of single shell C-S particles that were formed with 1k, 5k and 20k ppm of N, P_1 and P_2 shell particles. The photographs clearly show that, in the case of the PcP_1 20k particles which was formed from 20 kppm of P_1 shell particles, the surface is remarkably rougher than those of two other types of C-S particles. The result presumably comes from the larger particle size P_1 particles; P_1 particles (diameter; 100 nm), which are 30 times larger than the N or P_2 particles (diameter < 3 nm), tend to coagulate during the precipitation and form the remarkable rough surface on the Pc core surface. The result suggests that the smaller size shell particles are an important factor to obtain the smoother C-S particle surface.

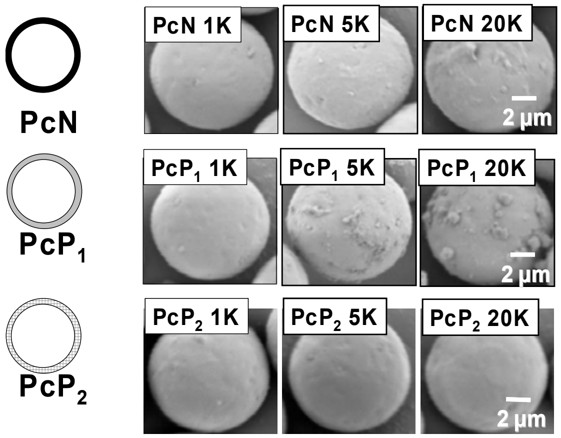

Fig.3 SEM photographs of three types of single shell C-S particles

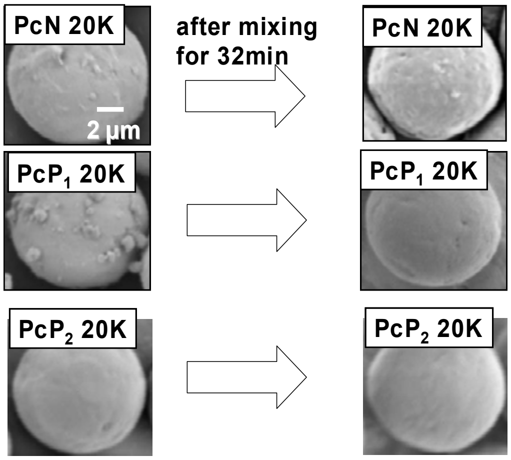

Fig.4 SEM photographs of three single shell C-S particles after mixing with carrier particles

SEM observation after mixing with carrier particles

The SEM photographs of PcN, PcP$_1$, and PcP$_2$ single shell C-S particles after mixing with carrier particles for 32 min. are shown in fig.4. It is remarkable that the surfaces of all three types of C-S particles are turning into smoother surfaces by the mixing operation with the carrier particles.

Tribo-charging characteristics in PcN single shell particles

Fig. 5 shows the tribo-charging characteristic curves of the PcN single shell C-S particles, indicating the amount of tribo-charge *q/m* as a function of mixing time. When the characteristic curves are compared with the reference characteristic curve, which was obtained for the Pc core particles, all the curves shift toward the negative charge region. The amount of negative charge shift of the curves increases with the increase of the amount of N particles on the Pc core surface.

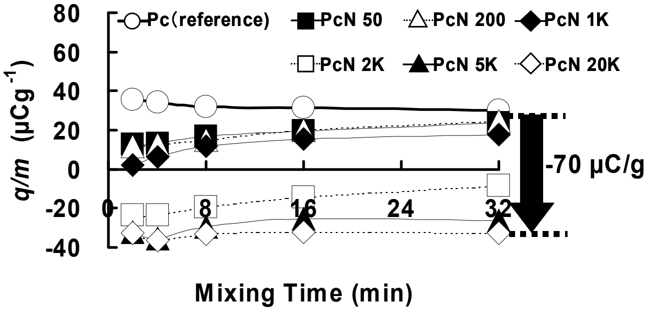

Fig.5 Tribo-charging characteristics for PcN single shell particles

Fig. 6 shows the relationship between the amount of negative charge shift and the amount of N particles that form the shell layer on the Pc core surface. The charge shift draws to an end when the amount of N particles on the Pc core surface exceeds 5 kppm. The ultimate amount of negative charge shift to be obtained from the PcN particles with more than 5 kppm of N particles is estimated to be about −70 μC/g.

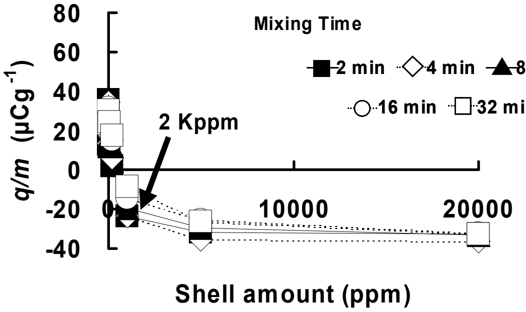

Fig.6 Relation between amount of negative charge shift and amount of N particles on the Pc core surface.

According to the ideal model for the PcN particles, the amount of N particles required to completely cover the Pc core surface is calculated to be about 1 kppm. However, the amount of N particles that is necessary for realizing charge shift saturation, which is considered to achieve a complete coverage by the shell layer in real PcN particles, is estimated to be larger than 2 kppm, since the experimental result of fig. 6 shows that, in the case of real PcN particles, the shell layer is formed form the coagulated N particles and require an incresed amount of N particles to cover the whole Pc core surface completely.

In Fig. 5, the amounts of tribo-charge *q/m* on PcN particles with more than 5 kppm N particles stay constant and show only a small variation with the mixing time. The result appears to come from the fact that the shell layers formed from N particles are durable enough even mixed with carrier particles for a prolonged time of 32 min.

Tribo-charging characteristics in PcP$_1$ single shell particles

Fig. 7 shows the tribo-charging characteristic curves of the PcP$_1$ single shell C-S particles. When the characteristic curves are compared with the reference characteristic curve, which was obtained for the Pc core particle, the curves obtained by using the PcP$_1$ 50, PcP$_1$ 200, and PcP$_1$ 1k particles shift slightly toward the positive charge region. However, the curves obtained from the PcP$_1$ particles which were formed from 5k and 20 kppm P$_1$ particles shift toward the negative charge region. The results may relate to the large, brittle and coagulated P$_1$ particles that cover the Pc core particle surface. During the mixing operation with carrier particles, the coagulated P$_1$ particles may be easily peeled off and transfered to the carrier particle surface to reduce the amount of tribo-charge *q/m*. This tendency is remarkable for the PcP$_1$ particles with more than 5 kppm of P$_1$ particles. As shown in the SEM photographs in Fig.4, the large coagulated P$_1$ particles on the PcP$_1$ 20k particle surface are thoroughly removed off after 32 min mixing with the carrier particles.

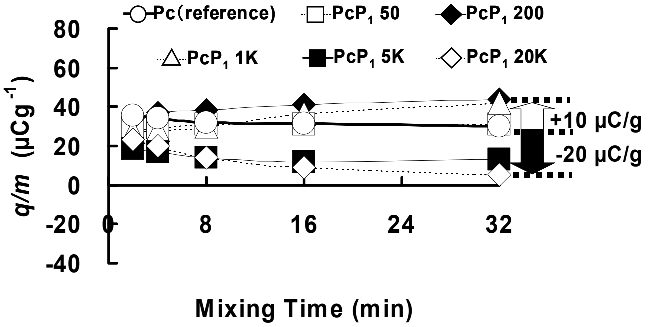

Fig.7 Tribo-charging characteristics for PcP$_1$ single shell C-S particles

Tribo-charging characteristics in PcP$_2$ single shell particles

Fig. 8 shows the tribo-charging characteristic curves of the PcP$_2$ single shell C-S particles. When the characteristic curves are compared with the reference characteristic curve, which was obtained for the Pc core particle, all the curves shift toward the positive charge region. The amount of positive charge shift of the curves increases with the increase of the amount of P$_2$ particles on the Pc core surface. The charge shift almost comes to an end when the amounts of P$_2$ particles on the PcP$_2$ particle surface exceed 5k ppm; in Fig. 8, the amounts of tribo-charge *q/m* on PcP$_2$ particles which have the P$_2$ particles of more than 5 kppm are kept at 35μC/g and show little change with the mixing time.

The results show that the shell layers formed from P$_2$ particles maintain enough durability even mixed with carrier particles for a time as long as 32 min.

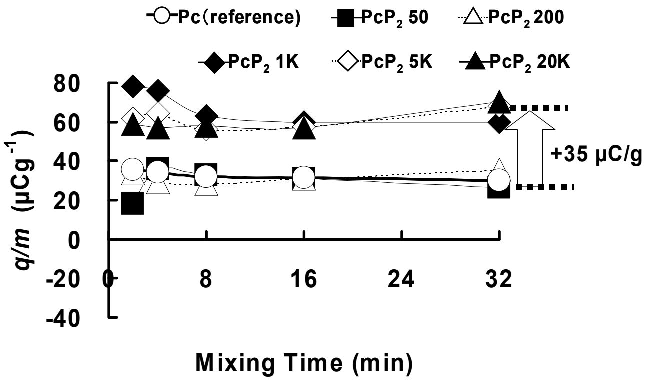

Fig.8 Tribo-charging characteristics for PcP_2 single shell C-S particles

Tribo-charging characteristics in $PcNP_1$ double shell particles

Tribo-charging characteristic curves of the $PcNP_1$ double shell particles are shown in Fig. 9. When the characteristic curves are compared with the characteristic curve of PcN 5k particles (see Fig. 5), which are used as a core to prepare the $PcNP_1$ double shell particles, all curves shift toward the positive charge region. The amount of positive charge shift increases with increase of the amount of P_1 particles on the PcN 5k core surface.

It seems that the coagulated and brittle P_1 particles on the $PcNP_1$ particle surface affect the charging characteristics of the $PcNP_1$ particles; in the SEM photographs for a $PcNP_1$ 20k particle in Fig. 4, the coagulated P_1 particles on the surface are thoroughly peeled off after 32 min mixing with carrier particle.

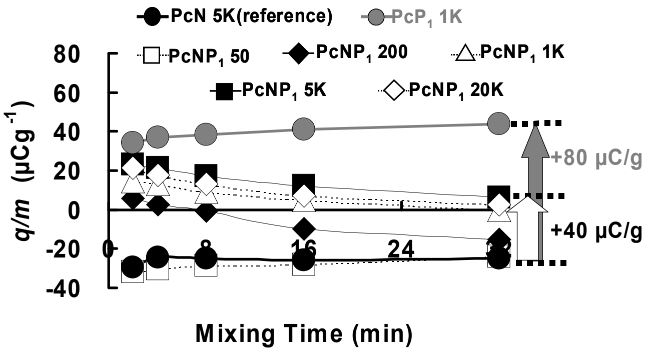

Fig.9 Tribo-charging characteristics for $PcNP_1$ single shell C-S particles

Tribo-charging characteristics in $PcNP_2$ double shell particles

Fig. 10 shows the tribo-charging characteristic curves of the $PcNP_2$ double shell particles. When the characteristic curves are compared with the characteristic curve of PcN 5k particles (see Fig. 5), which are used as a core to prepare the $PcNP_2$ double shell particles, all curves shift toward the positive charge region. The amount of positive charge shift increases with increase of the amount of P_2 particles on the PcN 5k core surface. The charge shift almost draws to an end when the amounts of P_2 particles on the PcN 5k core surface exceed 5k ppm. The ultimate amount of positive charge shift at 32 min mixing time, which is obtained from the $PcNP_2$ particles with more than 5 kppm of P_1 particles, is estimated to be about 100 μC/g.

The tribo-charging characteristic curve obtained from the $PcNP_2$ 5k particles nearly coincide with the curve obtained from the PcP_2 5k particles (see Fig.8). The fact shows that, in the $PcNP_2$ double shell particles, the tribo-charging characteristics are determined by the charging characteristics of the top shell formed from the P_2 particles.

As shown in Fig. 10, the amount of *q/m* on the $PcNP_2$ particles with more than 5 kppm P_2 particles keeps a value of +35 μC/g and shows little variation with the mixing time. The result probably comes from the fact that the top shell layer formed from the P_2 particles persists even mixed with carrier particles for 32 min.

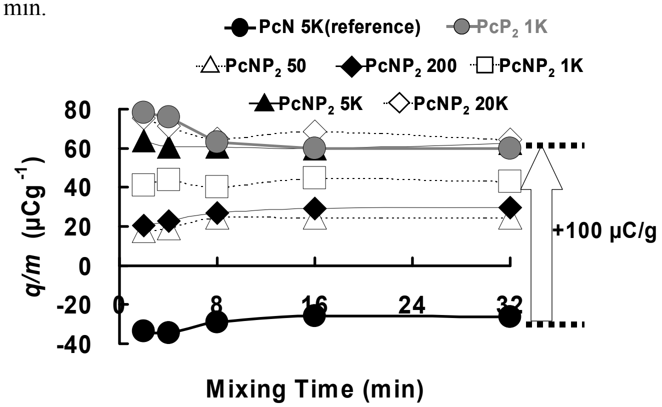

Fig.10 Tribo-charging characteristics for $PcNP_2$ single shell C-S particles

Conclusion

Using the particle size of less than 3nm copolymer shell particles, C-S particles with an ultra-thin shell layer having a thickness of less than 20 nm were prepared. The ultra-thin shell layer determines the tribo-charging characteristics of the C-S particles. By selecting the types and amounts of the shell particles, the polarity and the amount of tribo-charge are accurately controlled. Double shell particles in which an upper uniform ultra-thin shell layer was formed on the single shell C-S particle surface were also prepared. The upper shell also determines the charging characteristics as seen in the shell layer in the single shell C-S particles.

The results suggest that the ultra-thin shell layer will be a useful tool to investigate or control the surface structure and surface properties of the C-S particle surface.

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