

Effect of Functional Groups on the Triboelectric Charging Property of Polymer Particles

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SYNOPSIS

Triboelectrification of small polymer particles (< 10 microns) in which various functional groups are introduced by addition of substituted comonomers is studied. The particles are produced by suspension polymerization and mechanical crushing of larger particles. The effect of the different production methods on the particle is described. The particles produced by the polymerization method have a spherical shape with a smooth surface, and those produced by the crushing method have an irregular shape. Studies show that particles that have easily ionizable functional groups are charged more effectively. It is believed the ion-transfer route is the dominant mechanism in the triboelectrification charging of the particle. The magnitude of charge becomes saturated after 0.5% addition of substituted comonomers in the particle. The particles produced by the polymerization method have a tendency to be charged effectively compared with those produced by the crushing method. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The triboelectrification of polymer particles is an important component for the process of electrophotography and for electrostatic paint application. Micron-sized polymer particles have attracted great interest from informational industries, especially in the field of the electrophotography. Triboelectrification is one of many very important properties for the toner particle. In spite of the importance of the triboelectrification property, only a few have reported the relationship between the sign and magnitude of the charge and the chemical structure of the particle material. A small number of reports do show limited qualitative rankings of various materials.¹⁻³

We report triboelectrical charging data of micron-sized polymer particles in which various chemical functional groups are introduced. The particles are produced by suspension polymerization and the me-

chanical crushing method; the effect of these different methods is also described.

EXPERIMENTAL

Preparation of Polymer Particles

Polymer particles were made by a suspension polymerization method or by a mechanical crushing method.

Polymerization Method

General procedures for the preparation of polymer particles by suspension polymerization were carried out as follows: A monomer phase was prepared by adding one of the comonomers listed in Figure 1 and 2,2'-azobis(2,4-dimethylvarelonitrile) (2.4 g) as a radical initiator to a mixture of styrene and *n*-butyl acrylate (60 g, 8 : 2 ratio by weight). The concentrations of the comonomers were varied per reaction (0.1, 0.5, 1.0, and 2.0% by weight).[†] An aqueous

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[†] Compound V was not completely dissolved in the monomer phase at the concentration level of 2%.

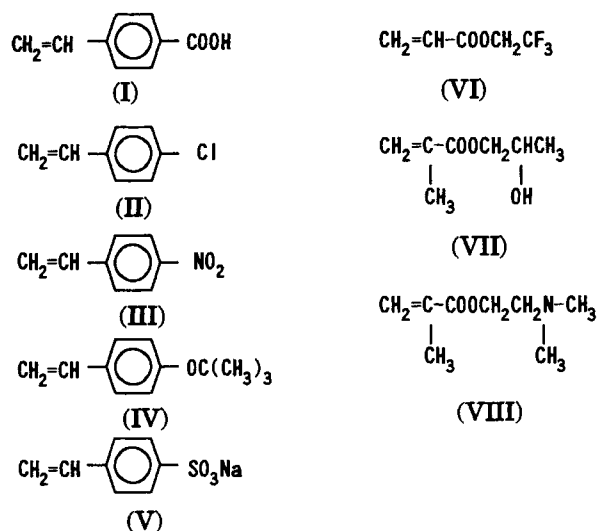


Figure 1 Structure of substituted comonomers.

phase was prepared by adding calcium phosphate (5% by weight) to an aqueous solution of 0.02% sodium dodecylsulfate.

The aqueous (240 g) and the monomer (60 g) phases were placed together in a 500 mL separable flask, dispersed using a homogenizer (Homomixer Type M, Tokushu Kikakougyou) at 12,000 rpm for 1 min. A portion (40 g) of the resulting dispersion was transferred into a 50 mL glass tube (30 mm i.d. and 60 mm height) and heated in a water bath to 60°C for 4 h, followed by an additional 3 h at 80°C. During polymerization, no agitation was employed over a period of the polymerization.^{4,5,†}

Polymer particles formed were washed with 1N nitric acid and then thoroughly washed with deionized water to remove any residual calcium phosphate from the particles' surface. After the washing, the polymer particles were dewatered using a centrifuge and dehydrated overnight at 35°C under reduced pressure (20 mmHg) in a vacuum oven.

Mechanical Crushing Method

Irregularly shaped polymer particles were made by the mechanical crushing of larger particles. A monomer phase was prepared by procedures similar to those described in the above section, except that all polymerizations were run with 2.0% of comono-

mers. An aqueous phase was also prepared just as described in the above section.

A 1 L two-necked flask equipped with a mechanical stirrer (a four-bladed turbine, 50 mm diameter) and a reflux condenser was charged with 300 g of the monomer phase and 600 g of the aqueous phase. The combined phases were agitated (300 rpm) and heated to 60°C for 4 h, followed by an additional 3 h at 80°C.

After thorough washing and drying, the polymer particles were spherical in shape with particle diameters over 200 microns. These particles were mechanically crushed using a pneumatic jet mill (Labojetmill, Nihon Pneumatic Kougyou) until particle diameters were reduced to those comparable with the polymerization method. The air-stream pressure in the mill was controlled in the range of 3–4.5 kg/cm².

Reagents

Styrene and *n*-butyl acrylate were reagent grade and treated with 0.1% aqueous sodium hydroxide to remove the inhibitor. Other materials were reagent grade and used without further purification. Deionized water was used in the aqueous phase for suspension polymerization.

Triboelectric Charging

Polymer particles were triboelectrically charged by extended mixing with a surface-oxidized iron powder. The polymer particle (1.5 g) and the iron powder (STV-25, 75 μm, Powdertech, 48.5 g) were placed in a 100 mL polypropylene bottle. The bottle was rotated on a pot mill at 100 rpm for 30 min. In order that moisture adsorbed on the materials was equilibrated with that in the environment, the polymer particles, the iron powder, and the bottle were kept at least for 24 h in a chamber where the relative humidity and temperature was controlled (65%, 25°C). The triboelectric charge of the polymer particles was measured using a Faraday gauge (Blowoff Powder Charge Meter, Toshiba Chemical). The triboelectrical charging experiments were carried out under a constant environment (at 65% relative humidity and 25°C).

Molecular Properties of Polymer Particles

Molecular weights were determined on a Waters M600 chromatograph equipped with a UV detector and a System Instrument Co. data processor. The detection wavelength was 268 nm, which corresponds to the absorption maximum of polystyrene.

[†] Agitation leads to break up and coalescence of monomer droplets in suspension polymerization, resulting in wide particle-size distributions or agglomeration. The process of the droplet coalescence was negligible and the droplets are considerably stabilized when the size of the monomer droplets is small (< 10 microns) and uniform. In our experiments, the combination of high shear homogenizing and proper droplet stabilization leads to effective stabilization of droplets and to small particles.

The column used was a Shodex GPC KF-80M packed with polystyrene gel. Calibration of the column was performed using standardized polystyrenes supplied by Showa Denko.

Particle Size

Particle size and distribution were determined on a TAI Coulter device by Coulter Electronics Inc. The aperture size on the tube for the Coulter analysis was 75 microns in diameter.

Electron Microscopy

Electron microscopic analysis was carried out on a JEOL JSM-T22A scanning electron microscope.

RESULTS AND DISCUSSION

Particle Characterization

Figure 2 shows particle-size distributions among the polymer particles made by the two methods: the polymerization and the mechanical crushing methods. The addition of comonomers except for VIII had no significant effect on the particle-size distribution among the polymer particles produced. The shape and surface appearance of the particles are shown in Figure 3. Two SEM photographs in Figure 3 illustrate the outstanding differences in the morphology between the polymer particles produced by the polymerization method and those by the mechanical crushing method.

Molecular Weight Distribution

The addition of comonomers does not significantly affect the molecular weight distribution (Fig. 4).

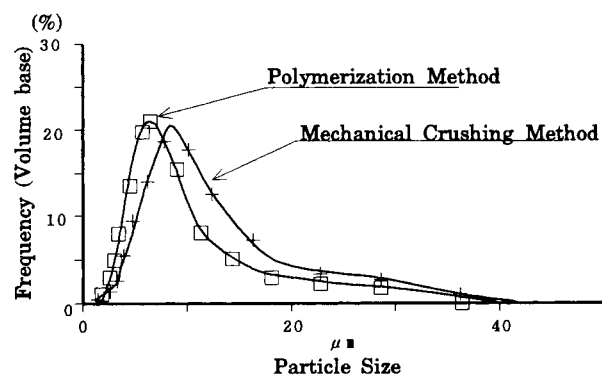


Figure 2 Particle-size distribution and mean particle size (volume mean): polymerization method, 6.31 μm ; crushing method, 7.50 μm .

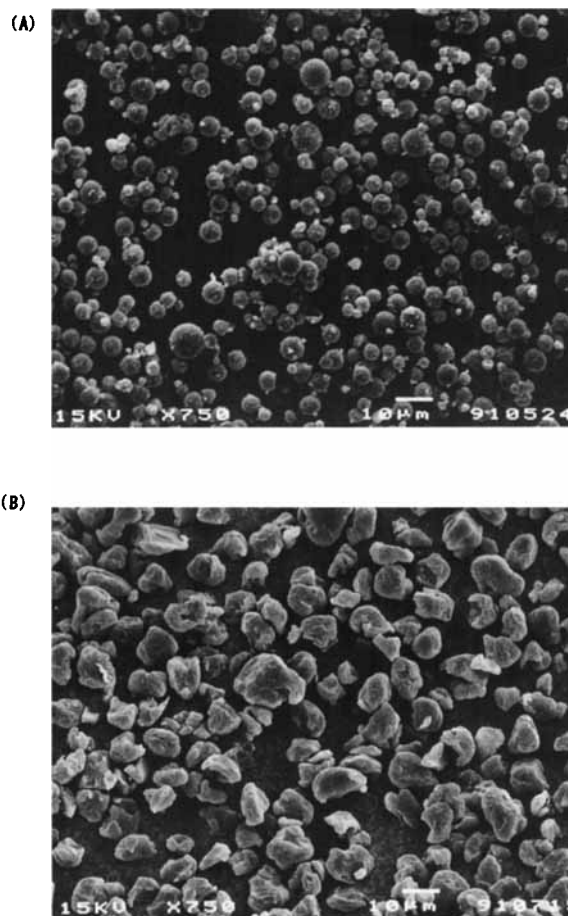


Figure 3 Photograph of particles: (A) polymerization method; (B) mechanical crushing method.

This may suggest that the addition of such functionalized comonomers does not alter the course of polymerization. Plausible reasons for this are the low concentration of the comonomers added and the relatively high concentration of initiator.

Effect of Functional Groups on Triboelectric Charging Property

Figure 5 shows the triboelectrical charging property of functionalized polymer particles produced by polymerization in the presence of one of the comonomers listed in Figure 1. Both comonomers I and V gave polymer particles having a definite negative charge on the frictional contact with iron powder. On the other hand, positively charged particles are obtained when the comonomer is VIII. Polymer particles produced with other functionalized comonomers shown in Figure 1, however, show only small changes in triboelectric charge properties. Polymer particles obtained from polymerization in the absence of any functionalized comonomers have

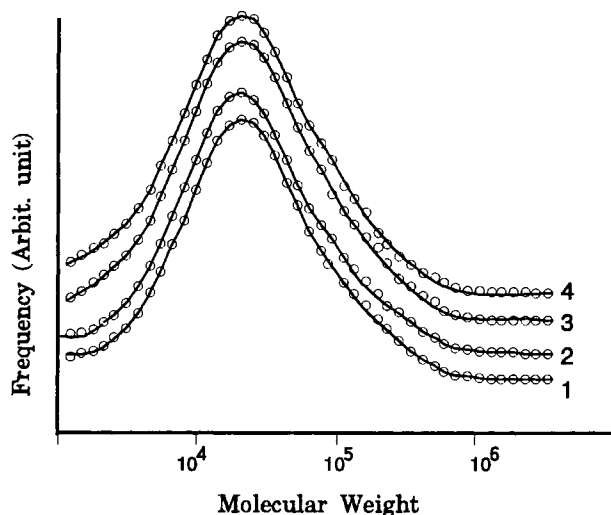


Figure 4 Molecular weight distribution with substituted comonomers (1% by wt): (1) I; (2) II; (3) VI; (4) VIII.

a slight positive charge (ca. $16 \mu\text{C/g}$). Therefore, comonomers with other functionalities except for carboxyl, sulfonate, and dimethylamino ester can be considered inert toward the triboelectrification.

As described above, the presence of comonomers I, V, and VIII have an effect on the triboelectric charging properties of the polymers produced. Since it may be possible that this effect could be attributed to the adsorption of the comonomers on the particle surface, the particle produced with I was thoroughly washed with methyl alcohol and the triboelectric charge measured. The charging data for the particle showed no difference from the previous data. The charge properties, therefore, are derived from the character of the particle surface and not from any adsorbed comonomer I on its surface.

Although a relationship between the chemical structure of materials and their triboelectrification has not yet been established, Oguchi⁶ observed a good linear relationship between the electronegativity of metal ions and the magnitude of the triboelectric charge. For this study, about 40 metal oxides were subjected to triboelectrification with iron powders. Given the results, they proposed an electron-transfer mechanism to correlate their observations. Gibson^{7,8} also found that the logarithm of the magnitude of the triboelectric charge had a good linear correlation to Hammett's sigma value of substituents on polystyrene. The correlation indicates that the triboelectrification phenomenon is solid-state electrochemistry, whereby one molecule loses an electron to another through physical contact.

The experimental data in Figure 5 show that the magnitude of charges of the particles are collected

on the effectively charged region or on the almost no charged one, indicating that there may be no functional correlation between the magnitude of charge and a physical constant such as Hammett's sigma value.

The effective functional groups to the charging in our study (I, V, and VIII) are the groups that are easily ionized by donating or accepting ions. This suggests that the ion transfer performs the triboelectric charging. The environmental condition during the charging experiments allowed for adsorption of extraneous materials (moisture, oxygen, nitrogen, etc.). These materials could have collected on the surface of the polymer and iron particle. In addition, the high surface area of small particles may enhance any effect on the particles. The extraneous materials and high surface area could provide a good source for transferring ions. These adsorbed materials may have the role of the charging site on the polymer particles.

Figure 6 shows the dependence of the comonomer concentrations on the magnitude of the triboelectric charge of the polymer particles. The magnitude of charge is saturated at a comonomer concentration of 0.5%. The actual charging site of the polymer surface may not be localized at each functional group, but may encompass some range around it. The limited number of functional groups could effectively cover the particle surface with potential charging sites.

The triboelectrification charging depends upon physical contact. The shapes of the particles could be a significant factor that effects triboelectrifica-

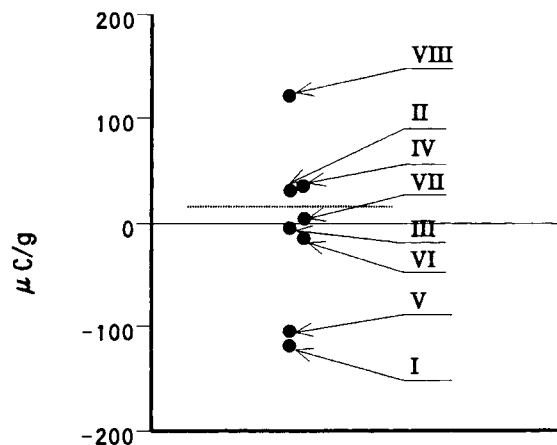


Figure 5 Sign and magnitude of tribocharge of particles with substituted comonomers. Concentration of comonomers: 1%. Roman numbers correspond to Figure 1. Dotted line represents charge of particles with no addition of comonomers.

tion. An irregularly shaped particle yields multiple contacts between particles, whereas a single contact is realized between spherical particles. The efficient contact between particles irregularly shaped may have some effect on the magnitude of the charge. Table I shows the magnitude of the charge on the irregularly and spherically shaped particles.

The absolute magnitudes of charges on the irregularly shaped particles are reduced compared to those of spherically shaped particles. This phenomenon is derived from the difference in the density of functional groups at the particles' surface. In a suspension polymerization, the aqueous affinity of comonomers could cause migration of the comonomer to the surface of the particle during droplet formation and polymerization.⁹ Subsequently, the comonomers delocalize at the particle surface. These functional groups at the surface can then effectively contribute to triboelectric charging compared to those inside the particles.

The irregularly shaped particles were produced by mechanical crushing. This method took the original polymer surface that had a concentrated functional group on it and broke it away. The newly formed surface contains less of the functional group, which resulted in lower charge development.

CONCLUSIONS

The effect of functional groups in small polymer particles (< 10 microns) on the triboelectric charging property was studied. The polymer particles are charged by rubbing against a surface of oxidized iron powder. The functional groups are introduced into the polymer particle by addition of functionalized comonomers.

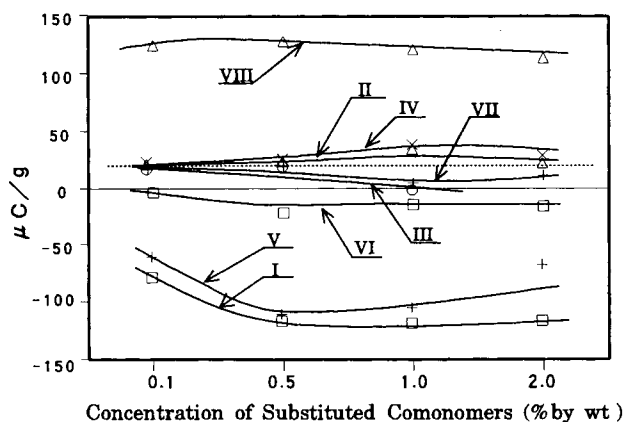


Figure 6 Effect of concentration of substituted comonomers on charge. Roman numbers correspond to Figure 1. Dotted line represents charge of particles with no addition.

Table I Magnitude of Charge of Spherical and Irregularly Shaped Particles

Additive Comonomers	Spherical Particles	Irregular-shaped Particles
I	-115.7	-56.2
II	+18.5	+6.2
III	^a	+4.3
IV	+25.2	-8.0
V	-66.8	-7.5
VI	-16.8	-4.5
VII	+10.8	-6.3
VIII	+113.0	+84.5
No addition	+16.0	

MicroCoulomb per gram. Concentrations of additive monomers are 2%.

^a Polymer particles aggregated for low conversion of polymerization.

It was observed that easily ionized functional groups provide an effective triboelectric charge. It is considered that the ions have an important role in charging, in which the ion transfer may be the dominant mechanism for triboelectrification.

The magnitude of charge is saturated at the concentration of 0.5% of the functionalized comonomer. The absolute magnitude of the charge on the particles produced by the suspension polymerization and mechanical crushing methods were compared. Results found that the suspension polymerization method was more effective in charge development. The observed difference is believed to be caused by the density of functional groups present at the polymer particles' surface.

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