

# Preparation of Pigment–Polymer Hybrid Particles for Plastic Colorants by Dry-Impact Blending Method

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**ABSTRACT:** Dry-impact blending method was employed to prepare hybrid particles composed of fine particles of phthalocyanine blue and a coarse particle of low-density polyethylene (LDPE). A simple mixing in a Henschel-type batch mixer of the two kinds of particles, which were largely different in the size, in ambient temperature applying high stress, produced hybrid particles, where the fine particles are distributed on the surface of the core particle. The surface appearances and the cross-sectional views of the particles were observed by scanning and transmission electron microscopy. It was revealed that the hybrid particles exhibited a capsule formation with the LDPE core coated with the phthalocyanine layer, where the phthalocyanine fine particles were embedded in the LDPE core particles. The hybrid particles thus prepared helps fine dispersion of the pigment into the LDPE matrix, and the pigmented LDPE sheet shows excellent color quality. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1762–1772, 1999

**Key words:** pigment; colorant; dry-impact blending; polyethylene; phthalocyanine

## INTRODUCTION

For coloring of plastics, pigment additives, such as titanium dioxide white, cadmium yellow, iron oxide red, carbon black, or phthalocyanine blue, are incorporated into a base polymer. Such color additives are available on the market in the form of color paste, color powder premix, or a color masterbatch. Those products are concentrated mixtures of pigments in a carrier resin usually containing 10 times the proportion of pigments needed in the final products. Normally, final products contain pigments in the range from 0.05 to 3.0%. The most desirable property required as a colorant is the fine dispersion of pigments in the matrix polymer because the color quality given to a base polymer depends on the state of the dis-

persion of pigments.<sup>1</sup> Moreover, inadequate pigment dispersion would lead to warpage, shrinkage, poor surface smoothness resulting in subsequent printing difficulties, and loss of mechanical properties of base polymers.<sup>2</sup> The processibility of pigments, that is, how readily they can be dispersed to a required fineness, play a decisive role in the manufacture of plastic colorants. The goal is to embed pigments in the polymer matrix quickly and easily. To achieve fine dispersion of pigments, surface treatments or addition of a surfactant were employed frequently to alter pigment surface and allow better wetting to the polymer matrix. Those processes, however, sometimes involve wet processes, which are not the preferred way regarding economical and also environmental issues. Moreover, the addition of surfactants would lead to excessive gas evolution or plateout on the mold.<sup>3</sup> It is therefore required that colorants should contain no additives other than the pigment and the carrier resin.

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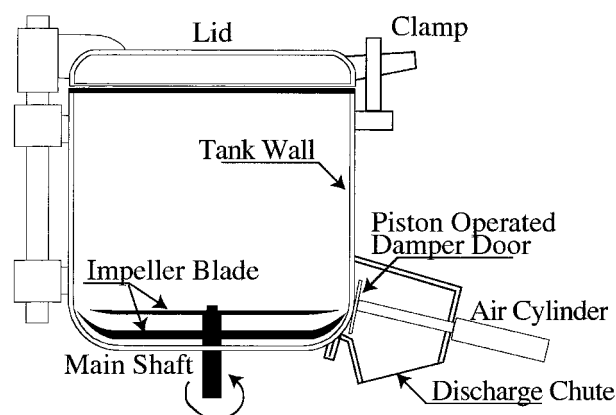
We here propose a novel process to achieve fine dispersion of a pigment into a base polymer by a dry process without help of dispersing agents. The dry-impact blending method was used in the investigation of surface modification technique of particles in the powder technology field.<sup>4-6</sup> Mixing fine and coarse particles with a mixer by applying high stress at ambient temperature gives an ordered mixture. The ordered mixture is the specific mixed state where the fine particles adhere to the surfaces of the coarse particles. This mixture can be obtained when large differences in particle size and favorable interactions exist between the two types of particles. This mixture can be modified to a novel type of particle of which physical characteristics are derived both from the fine (coating materials) and the coarse particles (core particles). This dry-impact blending method was developed to modify, coat, and hybridize particles with various materials. There were several reports on their applications in the cosmetic and pharmaceutical fields. For example, a skin foundation manufactured by this method is now commercially available,<sup>7</sup> and improvement of the dissolution rates of poorly soluble drugs by coating potato starch with them by using this method was also reported.<sup>4,5</sup>

We prepared hybrid particles composed of fine particles of a copper-phthalocyanine blue (CPB) pigment and core particles of low-density polyethylene (LDPE) by the dry-impact blending method, and the state of the ordered mixture was investigated by scanning and transmission electron microscopy (SEM and TEM, respectively). After that, we evaluated the dispersion of the CPB into the LDPE matrix by TEM, and also evaluated the color quality of the pigmented LDPE.

## EXPERIMENTAL

### Materials

The LDPE particle used as a core material was purchased from Sumitomo Seika Chemicals Co., Ltd. (Flo beads LE-1080, Osaka, Japan), of which average diameter is 6  $\mu\text{m}$ . As fine particles, CPB (FBK #3) purchased from Sanyo Color Works, Ltd. (Himeji, Okayama, Japan), polymethylmethacrylate (PMMA) purchased from Soken Chem. & Eng. Co., Ltd. (Chemsnow MP-1451, Tokyo, Japan; 0.15  $\mu\text{m}$  in diameter), and titanium dioxide ( $\text{TiO}_2$ ) purchased from DuPont (Ti-Pure, Delaware, USA, 0.23  $\mu\text{m}$  in diameter) were used.



**Figure 1** A schematic illustration of the Henschel mixer used in this study.

### Dry-Impact Blending Method

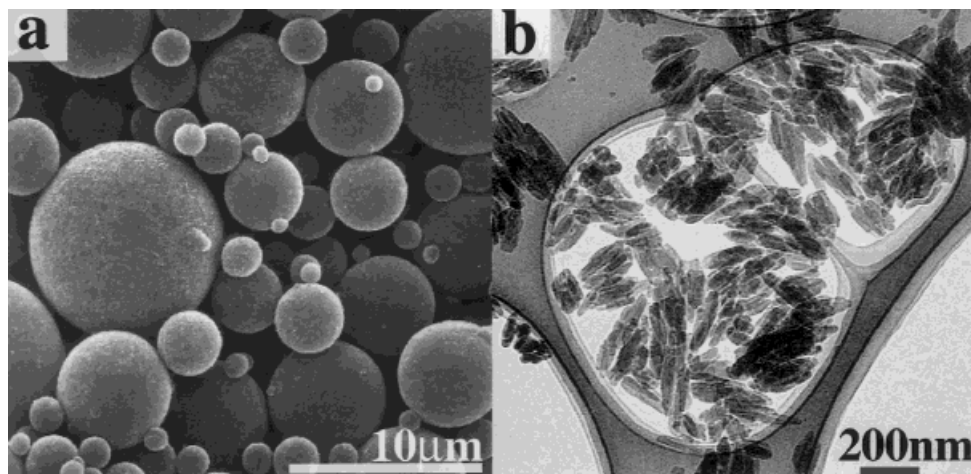
To produce the hybrid particles, the dry-impact blending with a Henschel-type batch mixer (FM40B, Mitsui Mining Co., Ltd., Tokyo, Japan) was performed. The schematic illustration of the mixer is shown in Figure 1, and the volume of the mixer is 40 L. Before loading into the mixer, the core LDPE particles and the fine particles were put into a plastic bag at a ratio of 100 : 6 (w/w), and the two kinds of particles were mixed by lightly hand shaking for 5 s. Then, the mixture of about 5000 g was charged into the Henschel mixer. The mixer was operated with an impeller blade at the speed of 120 m/s for 5 min. The powder mixture is fluidized in the chamber on air stream generated by the blade rotation at high speed. To avoid the increase of temperature by frictional heat, the inner surface of the chamber was cooled by a jacket through which cold water circulated. After the treatment, the powders were discharged from the discharge chute and collected.

### Preparation of the Pigmented LDPE Sheets

For the evaluation of the performance as colorants, the hybrid particles prepared as mentioned above and LDPE granules (Mitsui Chemical Corp., Tokyo, Japan; Mirason 402) were mixed with a two-roll kneader at 150°C. The sheets of the pigmented LDPEs of 0.2-mm thickness were prepared by compression molding at 150°C.

### Microscopy

For the observation of the surface appearances of the hybrid particles, SEM (XL-20, Philips) was



**Figure 2** (a) SEM photograph of the LDPE particles, and (b) TEM photograph of the CPB particles used in this study.

operated at an accelerating voltage of 30 kV with the samples coated with gold by an ion-sputtering machine.

To observe the cross section of the hybrid particles, TEM (Carl Zeiss EM902) was operated at an accelerating voltage of 80 kV. The particles were embedded in epoxy resin (Quetol 812) and cured at room temperature for 6 days. Then, thin sections with the thickness of about 100 nm were collected by cutting cryogenically at  $-100^{\circ}\text{C}$  on an ultramicrotome (Reichert Ultracut E) with a diamond knife. The dispersion of the CPB pigments in the LDPE sheets were also evaluated by TEM with the sections from the compression-molded sheets. Staining with  $\text{RuO}_4$  was employed for the purpose of the observation of the lamellar morphologies of LDPE.

The spherulitic texture of the pigmented and the nonpigmented LDPEs were characterized by an optical microscope with polarized light on an Olympus BH-2. Sections for the observation were cut from the molded sheets on a microtome.

#### Thermal Analysis of LDPE Sheets

For the characterization of the crystallization behavior of the pigmented and the nonpigmented LDPEs, differential scanning calorimetry (DSC) was performed by using a Perkin–Elmer DSC4 apparatus. The samples were initially heated in a nitrogen atmosphere from 30 to  $150^{\circ}\text{C}$  and were held at that temperature for 5 min. Then, the samples were cooled at the rate of 10 K/min to  $60^{\circ}\text{C}$ . Crystallization temperatures ( $T_c$ ) were obtained from the peak temperatures.

#### Evaluation of Color Quality

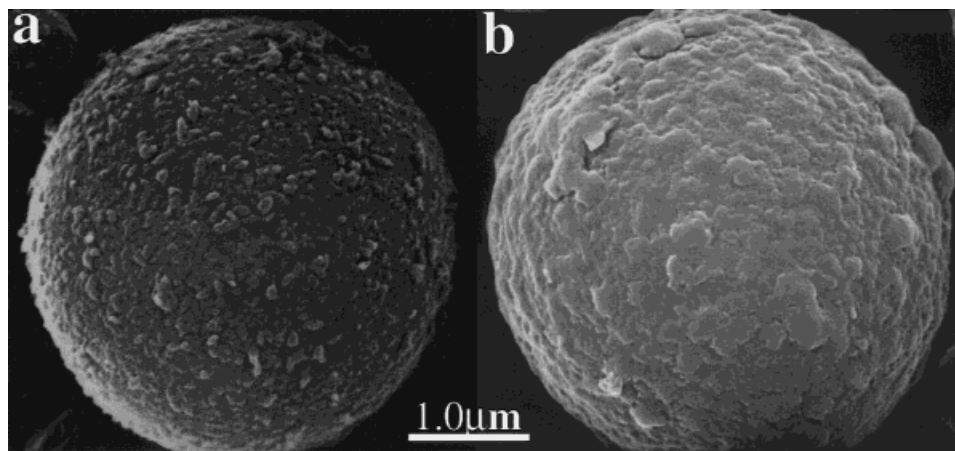
Optical clarity of the LDPE sheets was measured on the compression-molded sheets with 0.2-mm thickness. Haze of the sheets was measured with a Suga HGM-2DP-type haze meter.

Reflectance measurements of the pigmented LDPE sheets were carried out by using a spectrophotometer (Minolta CM-2002).

## RESULTS AND DISCUSSION

#### Structure of the Hybrid Particles

Figure 2(a,b) shows the photographs of the LDPE particles by SEM and the CPB pigments by TEM used in this study, respectively. The CPB for TEM observation was diluted with ethanol and dispensed onto a copper grid covered with micro-grid membrane. As shown in Figure 2(a), the size of the LDPE particles are varied in the range from about 1 to about  $10\ \mu\text{m}$  in diameter, but the surface is relatively smooth. Figure 2(b) shows that the original shape of CPB is rodlike and the size of the rod is approximately 200-nm across and 50-nm thick. The surface appearance of the hybrid particles of the LDPE core and the CPB fine particles are shown in Figure 3 as SEM photographs. Figure 3(a) is the particle obtained just after hand mixing in a plastic bag before loading into the mixer, and Figure 3(b) shows the surface appearance of a particle treated by the dry-impact blending after mixing in a plastic bag. Figure 3(a) indicates that, before loading into the mixer, the



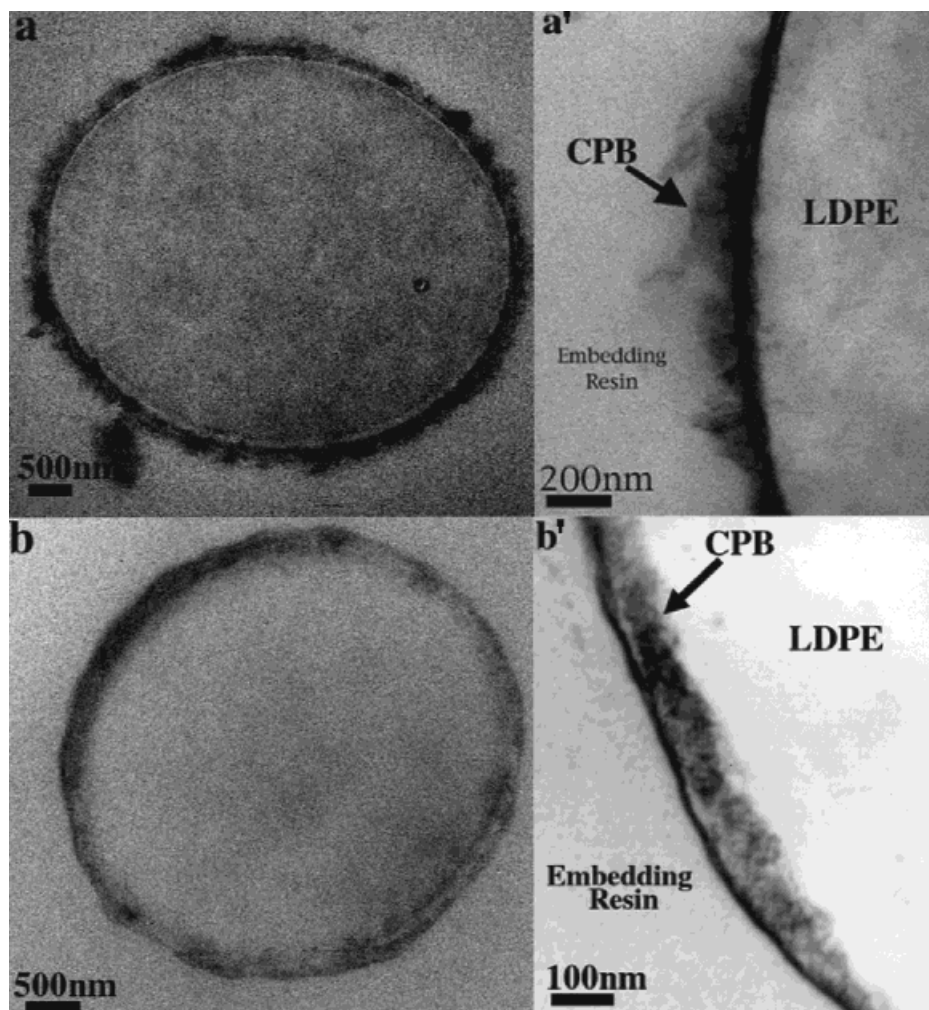
**Figure 3** SEM photographs showing the surface appearances of the hybrid particles composed by CPB fine particles and a LDPE particle. (a) The hybrid particle after roughly mixing the mixture in a plastic bag, and (b) the hybrid particle after the dry-impact blending.

small CPB particles are fixed and uniformly distributed on the LDPE surface. The CPB particles fixed on the LDPE surface seem larger than the single CPB, as shown in Figure 2(b), indicating that the agglomeration of the CPB occurs. However, the surface appearance of the particle roughly mixed in a plastic bag indicates that an ordered mixture can be easily obtained only by applying physical force with one's hand. The hybrid particles obtained by dry-impact blending, on the other hand, are distinctly different from that prepared by hand mixing in the surface appearance. After the dry-impact blending, the surface tends to be smooth, suggesting that the CPB particles coat the LDPE core in a layer over the surface.

The cross-sectional views of these two particles by TEM show more distinct difference of the hybridized state between them, as shown in Figure 4, where CPB gives dark contrast in the TEM photographs because it contains copper. Figure 4(a) shows the cross section of the particle prepared by hand mixing, and 4(a') is a magnified view of 4(a), focused on the surface of the LDPE particle, whereas Figure 4(b,b') show the preparation by the dry-impact blending. Even roughly hand mixed, the CPB particles can uniformly surround the LDPE core particle as shown in Figure 4(a), but the magnified view in Figure 4(a') indicates that they are simply fixed on the surface. The hybrid particles subjected to the dry-impact blending, on the other hand, exhibits the penetration of the CPB into the LDPE core as shown in Figure 4(b'). The depth of the penetration is about

100 nm, and the penetrated CPB does not remain in the original shape of the crystal formation as shown in Figure 2(b). This evidence suggests that the mechanical force applied to the CPB particles during the mixing, such as shear stress and impact force, overcomes the intermolecular forces holding the molecules together in a crystal form, and then the CPB crystal lattice is disrupted into fine pieces. During the fluidization of the mixed particles in the Henschel mixer, the hybrid particles in an ordered mixture, where the PCB fine particles adhere to the LDPE surfaces, collide with other particles, blade, and inner wall of the mixer. The mechanical forces given by such collisions and friction cause the distortion and disruption of the CPB crystal lattice and drive the fine CPB clusters into the inside of the core particles in a certain depth. The CPB clusters generated by the impact force are considered to be in a metastable state, which could be recovered to the stable crystal state in a normal situation. It can be assumed, however, that the CPB clusters are embedded in LDPE, and thus can be fixed for a long time.

Ishizaka et al. investigated the hybridization of a variety of drugs with potato starch used as a core material for the development of the drug delivery system.<sup>4</sup> They reported that the hybridized state was dependent on the physical properties of the drugs used as fine particles. We hence investigated the effect of the nature of fine particles on the hybridized state by the alteration of the CPB to  $\text{TiO}_2$  and PMMA. The hybrid particles prepared by the dry-impact blending composed by

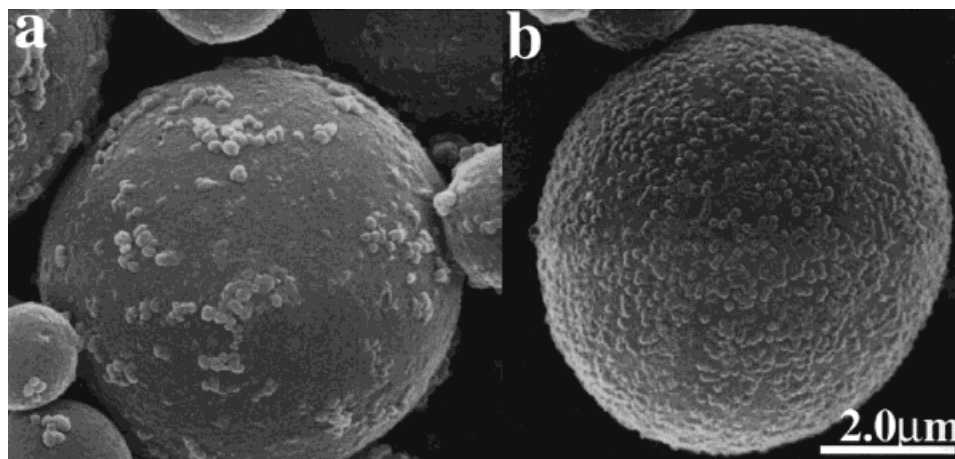


**Figure 4** TEM photographs showing the cross-sectional views of the hybrid particles. (a), (a') The hybrid particle prepared by hand mixing; (b), (b') the hybrid particle prepared by the dry impact blending. (a') and (b') are the magnified view of the corresponding photographs showing the surface of the particles.

TiO<sub>2</sub> and LDPE, and by PMMA and LDPE are shown in Figure 5(a,b), respectively. Although an ordered mixture can be obtained with these two combinations, it is obvious that the layers are not formed on the core surfaces. Ishizaka et al. mentioned that the heat of fusion of fine particles is related to the hybridized state rather than to the melting point, and they concluded that the mechanochemical phenomena are responsible for the hybridized state. That is, the mechanical energy applied to the fine particle, produced by the collision and the friction, changes the crystal formation of the fine particles to metastable states, and subsequently, they are formed in a layer or penetrate into core particles. In our case, in terms of the thermal stability, PMMA is much inferior to

CPB and TiO<sub>2</sub>, because the glass transition temperature ( $T_g$ ) of PMMA is ca. 100°C, whereas CPB and TiO<sub>2</sub> are stable at higher temperatures. However, the PMMA particles remain the original shape on the core surface. CPB is a molecular crystal, indicating that CPB is too brittle to be easily disrupted and distorted by mechanical energy rather than the ionic crystal of TiO<sub>2</sub>. Therefore, our results also suggest that the mechanochemical phenomena are dominant during the hybridization processes.

We evaluate the performances as colorants of the two types of hybrid particles composed by CPB and LDPE in the following sections, which have different states of the ordered mixture as described above. The one is the hybrid particles



**Figure 5** SEM photographs showing the surface appearances of the hybrid particles composed by (a)  $\text{TiO}_2$  small particles and a LDPE core particle, and (b) PMMA small particles and a LDPE core particle prepared by the dry-impact blending.

prepared by hand mixing (HP-HM), and the other is prepared by the dry-impact blending (HP-DIB).

#### Dispersion of CPB Pigments in LDPE

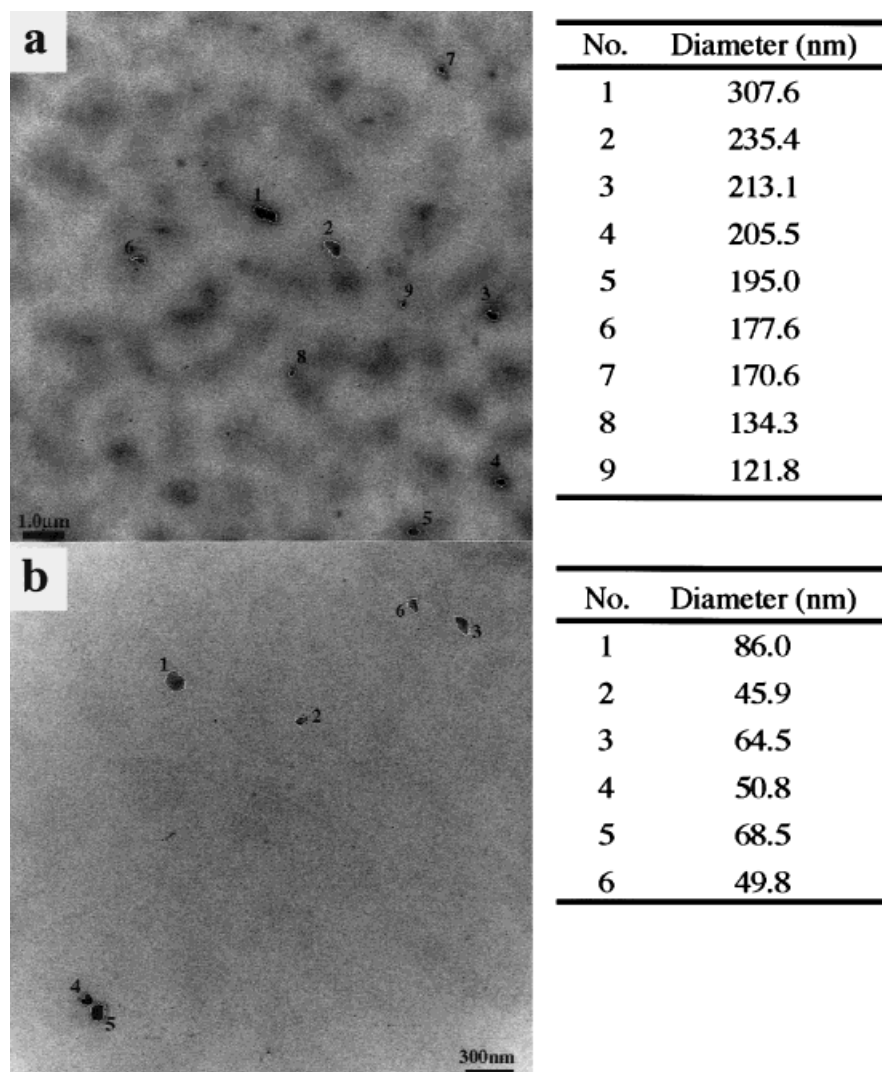
Each hybrid particle was blended at 0.88 wt % with LDPE where the CPB pigment contains 0.05 wt %. Figure 6(a,b) are TEM photographs comparing the degree of dispersion of the CPB pigment in the LDPE matrix pigmented by using HP-HM and HP-DIB, respectively. Because the concentration of the pigment is quite low, a few pigment particles appear in each image, but the dispersion of the pigment in the LDPE matrix with HP-DIB is obviously much better than that with HP-HM. In Figure 6, the individual pigment particles are assigned numerically on the images, and the diameters of the corresponded particles are also shown in the tables. The diameters assigned to the each particle were determined as that of a circle of equivalent area. The size of the CPB dispersed in the LDPE matrix blended with HP-DIB ranges from ca. 50 to 100 nm, whereas the size is at least  $>100$  nm in the pigmented sheet with HP-HM. It can be noted that the CPB particle size dispersed in the LDPE matrix is smaller than the original CPB particles, as shown in Figure 2(b) when HP-DIB are used for pigmentation. As shown in Figure 4(b'), the CPB embedded in the LDPE core particles has no original crystalline form and are smaller than the original CPB particles, and therefore, it can be speculated that the CPB can be loaded with this state accompanied by the carrier LDPE core particles into the LDPE matrix during the blending.

#### Color Quality of the Pigmented LDPE Sheets

The pigmentation of LDPE sheets by the CPB by using the hybrid particles gave blue and transparent films. It was easily recognized by simple visual inspection that the pigmented LDPE sheet by HP-DIB gave better optical clarity compared with the pigmented sheet using HP-HM. The haze values of the compression-molded sheets with 0.2-mm thickness as a function of the weight fraction of the pigment are shown in Figure 7. This indicates that the addition of the pigment to LDPE decreases the haze value significantly, which means that the sheets have higher transparency. The hybrid particle prepared by HP-DIB decreases the haze value drastically with the small amount of CPB, and then it levels off by further addition, whereas HP-HM decreases the haze value gradually as an increase of the pigment content.

It is known that the optical clarity is affected by the spherulite size in semicrystalline polymers.<sup>8</sup> The results shown in Figure 7 suggest that the CPB acts as a nucleating agent for the LDPE crystallization. The crystallization behaviors characterized by DSC confirm that fact. Figure 8(a–c) shows the DSC cooling traces of the pure LDPE, the LDPEs pigmented by 0.05 wt % of CPB by using HP-HM, and by HP-DIB, respectively. The addition of the pigment increases the  $T_c$  by ca.  $5^\circ$ ; that is, a fast crystallization occurred, compared with the nonpigmented LDPE.

The spherulitic structures were observed by polarized optical microscopy (POM) and TEM to discuss the influence of the addition of the pig-

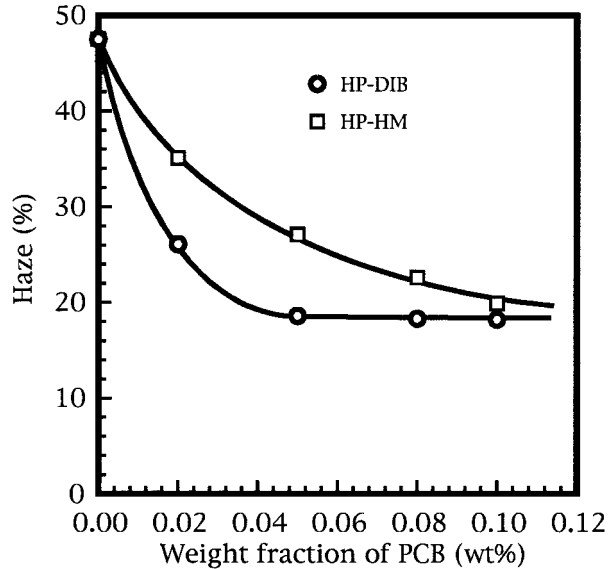


**Figure 6** TEM photographs showing the dispersion of the CPB pigment particles in the LDPE sheet. (a) Pigmented by HP-HM, and (b) pigmented by HP-DIB. The diameters of the individual particles assigned numerically in the images are shown in the tables.

ment on the structure of the LDPE matrix. Figure 9(a–c) shows the POM photographs of nonpigmented LDPE, a pigmented LDPE with 0.05 wt % of CPB by HP-HM, and a pigmented LDPE with the same fraction of CPB by HP-DIB, respectively. Also, the corresponding higher magnification TEM photographs are shown in Figure 9(a'–c') with unstained specimens, exhibiting the detailed spherulitic structures where the amorphous and crystalline regions give different contrasts. Apparently, the spherulite size of the pure LDPE is much larger than those of the pigmented LDPEs. This means that the addition of the pig-

ment decreases the spherulite size significantly (i.e., the nucleation density increases). Also, the LDPE pigment using HP-DIB exhibits finer spherulitic texture than that prepared by HP-HM. This means that the nucleation efficiency is higher in the pigmented LDPE by HP-DIB.

Higher magnification views by TEM with stained specimens with  $\text{RuO}_4$  allow us to observe the lamellar fine structures. Figure 10(a,b) shows the lamellar structures that appear in the pure LDPE and pigmented LDPE by HP-DIB, respectively. The fold surfaces of the lamellae are selectively stained and appear dark. Figure 10(b) im-



**Figure 7** Haze values of the pigmented LDPE sheets as a function of the weight fraction of CPB.

plies that the lamellae growth was radially initiated from a pigment particle. On the other hand, many short lamellar fragments are observed to be randomly arranged in the nonpigmented LDPE, as shown in Figure 10(a). The comparison of the lamellar morphologies indicates that the presence of the pigment affects the crystallization growth behavior of LDPE and consequently changes the lamellar arrangement.

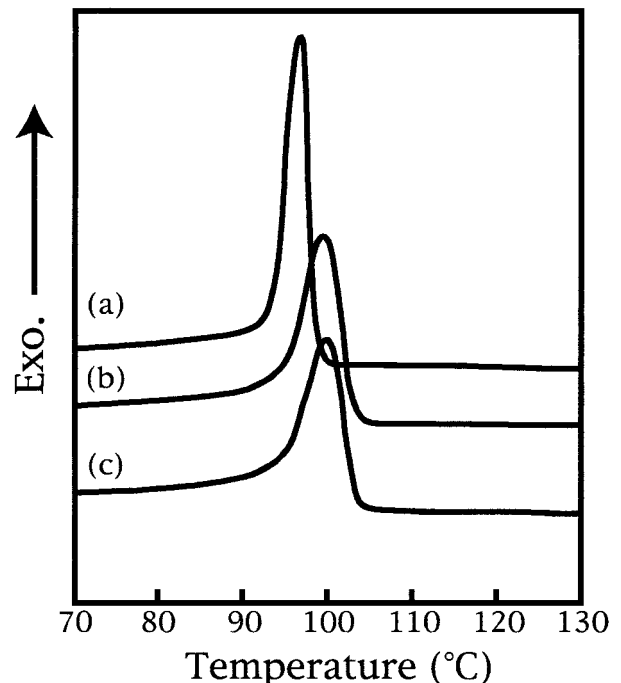
The dependence of the haze value on the fraction of the pigment shown in Figure 7 can be explained by taking into account the fact that the number of nuclei increases as the number of the pigment particles increases, and then consequently, the size of the spherulite is reduced. In the pigmented LDPE sheet by HP-DIB, the spherulite size decreases sufficiently to a specific size with a small amount CPB because of the fine dispersion, which is close to the wavelength of the visible light. On the other hand, a greater amount of CPB is required to reduce the spherulite size to the specific value due to the poor dispersion of CPB in the sheet with HP-HM.

To measure the spectral reflectance of the pigmented sheets, the samples must be completely opaque to obscure a background or a substrate. Hence,  $\text{TiO}_2$  was added at 0.45 wt % with the CPB into the LDPE. The two pigmented LDPE sheets by HP-DIB and HP-HM showed different color appearance, being detectable by simple visual in-

spection. The depth of blue color seemed to be higher in the sheet with the particles by HP-DIB rather than by HP-HM. In other words, HP-DIB gave a darker blue tone to the LDPE. To discuss the color appearance quantitatively, spectrophotometric measurements were carried out, and the reflectance curves are shown in Figure 11. Both sheets, however, give apparently no differences in the reflectance curves in all the range of wavelength, which shows the characteristic shapes of CPB.<sup>10</sup>

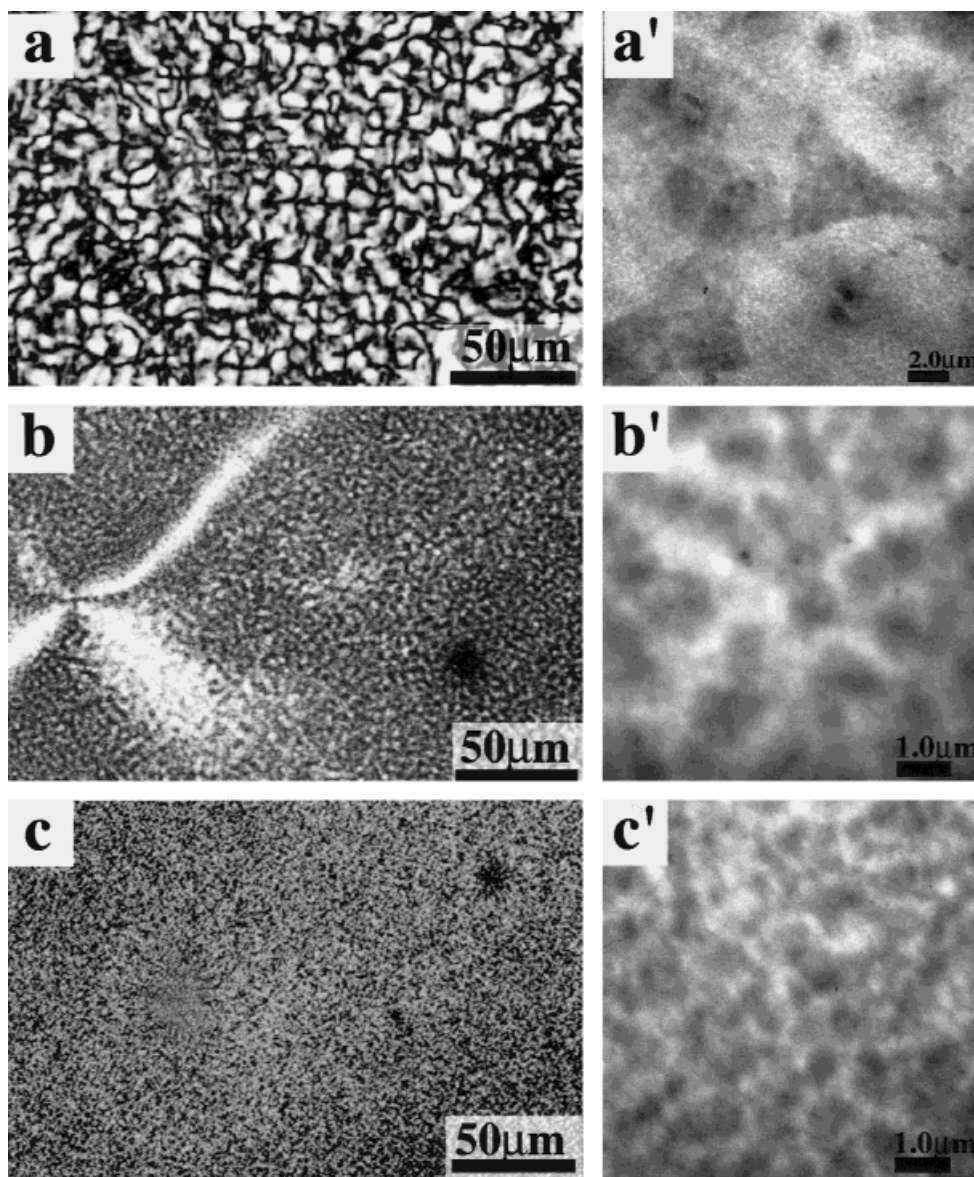
It is known that a spectrophotometric curve is not a description of what we see. The incident light impinging on pigment particles is scattered and absorbed. This behavior accounts for the color of materials; therefore, the observed color should be influenced by the particle size.<sup>11</sup> Many theories were described to relate the absorption and scattering of the particles at each wavelength to the subsequent effect on the observed color. Among them, the Kubelka–Munk theory (K–M theory)<sup>1</sup> is the simplest, describing a relationship between the reflectance, the absorption, and the scattering, given by

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (1)$$



**Figure 8** DSC cooling traces for (a) pure LDPE, (b) pigmented by HP-HM, and (c) pigmented by HP-DIB.

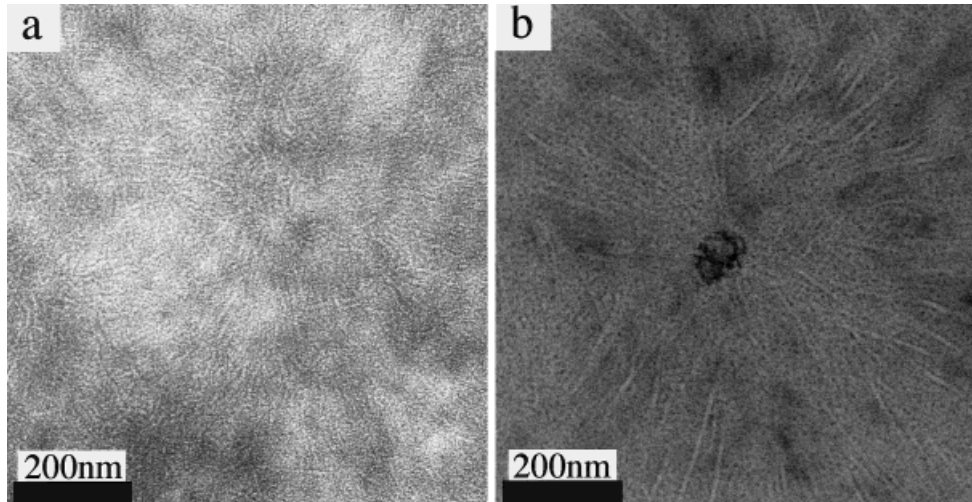




**Figure 9** POM photographs showing the spherulitic textures of the LDPE. (a) Pure LDPE, (b) pigmented by HP-HM, and (c) pigmented by HP-DIB. (a'), (b'), and (c') are higher magnification TEM photographs of the corresponded samples.

where  $R_\infty$  is the decimal fractional reflectance,  $K$  is the absorption coefficient, and  $S$  is the scattering coefficient. The K-M theory was widely applied to the evaluation of color characteristics and the color formulations. Figure 12 shows the Kubelka-Munk ratio,  $K/S$ , plotted against wavelength. The sheet pigmented by HP-DIB gives higher ratios of  $K/S$ , especially at wavelengths  $> 550$  nm. This can be interpreted as follows.  $\text{TiO}_2$  pigment has large  $S$  and small  $K$  values over the whole range of the wavelengths in visible light, meaning that  $\text{TiO}_2$

gives a strong scattering effect,<sup>11</sup> whereas the CPB has a conversed nature. Suppose that we add the CPB blue pigment into a white-pigmented sheet with  $\text{TiO}_2$ ; this would cause the increase of  $K$ , give high  $K/S$  ratios, and then lower the reflectance. Therefore, the results shown in Figure 12 indicates that HP-DIB has a higher efficiency for the blue pigmentation than HP-HM. Hence, it can be mentioned that the differences that appear in the  $K/S$  curves account for the visual impression of the color in the pigmented sheets.



**Figure 10** TEM photographs showing lamellar morphologies of (a) pure LDPE, and (b) the pigmented LDPE by HP-DIB containing 0.05 wt % of CPB.

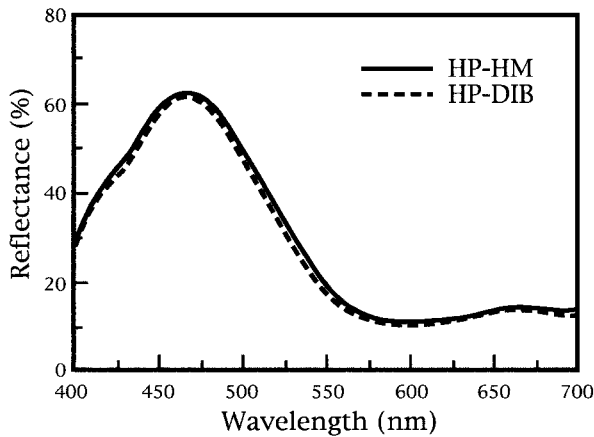
**CONCLUSION**

By the dry-impact blending method, the hybrid particles composed of CPB fine particles and a LDPE core particle were prepared. The state of the ordered mixture was investigated by SEM and TEM. It was revealed that the CPB fine particles are embedded in the LDPE particles at a depth of ca. 100 nm, and that the embedded CPB are finer pieces than the original crystal.

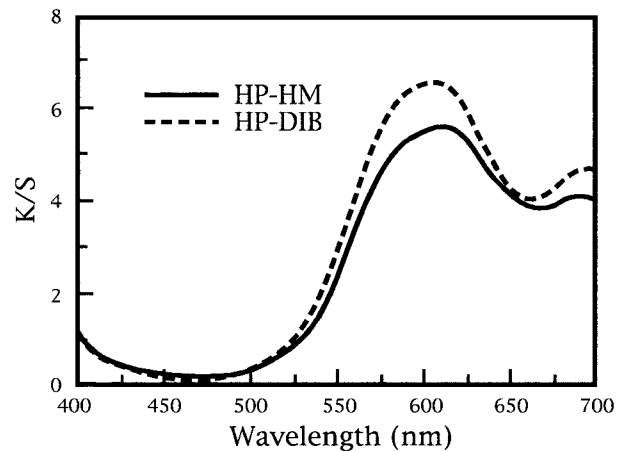
The hybrid particles thus prepared offer excellent dispersion of the pigment in a LDPE matrix. The attained particle size is <100 nm, which is smaller than the original CPB particles.

The pigmented LDPE sheet by HP-DIB exhibits good color quality; that is, it shows better optical clarity, and moreover, gives the dark blue tone when blended with TiO<sub>2</sub> and used as a hiding pigment. It was found that the pigment particle acts as a nucleating agent to decrease the spherulite size of LDPE. This contributes to the improvement of optical clarity to increase transparency of the sheet.

The dry-impact blending method is a simple and useful way to manufacture plastic colorants, considering that the fine dispersion of the pigment was achieved with no dispersing agents. Also, it is another advantage that this blending



**Figure 11** Spectrophotometric reflectance curves of the LDPE sheets pigmented by HP-HM and HP-DIB. CPB is contained at 0.05 wt %, and TiO<sub>2</sub> is contained at 0.45 wt % as a hiding agent.



**Figure 12** Kubelka-Munk ratios, *K/S*, plotted against wavelength for the LDPE sheets pigmented by HP-HM and HP-DIB-containing CPB at 0.05 wt %.

method can be performed at ambient temperature without the use of solvents.

The phenomenon that occurs during the blending is so complicated that the detail mechanism is still unknown, but the results obtained in this study suggest that the mechanochemical phenomenon is dominant in the formation of the ordered mixture as was mentioned in the previous works.

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