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Assistant effect of nano-$CaCO_3$ particles on the dispersion of TiO_2 pigment in polypropylene composites

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TiO_2 is extensively used in materials-coloring field as an excellent white pigment. An increasing interest focuses on the surface coating modification of TiO_2 in order to improve the application performance in polymer matrix [1–3]. Martin Arellano *et al.* studied the surface modification of TiO_2 powder and presented an evaluation method [1]. Noman S. Allen *et al.* investigated the photochemical and thermochemical behavior of TiO_2 pigments [2]. Nano-$CaCO_3$ is an important inorganic material whose toughening and strengthening functions in plastics have been verified [4–6]. In this paper, nano-$CaCO_3$ synthesized by a high gravity reactive precipitation method was employed as a new pigment dispersant, blending with TiO_2 and other additives to prepare complex master batches for use in the coloring of polypropylene (PP). The influence of the synergism of $CaCO_3$ and TiO_2 on the performance of colored PP products is discussed.

Nano-$CaCO_3$, TiO_2 and other additives were stirred uniformly in a high speed mixer followed by blending in a double roll plasticator. The blended sample was crushed and extruded in a single screw extruder to prepare nanosized complex color masterbatch, which was subsequently blended with PP resin in a plastic jetting-molding machine to yield colored products.

Whiteness measurements were performed by a TC–P II G Auto Color Difference Meter (Beijing Optical Instrument Factory, China, Hunter's L, a, b color space, 0/d geometrical conditions, 10° field of view, TW whiteness formula). Ultraviolet (UV) absorption characteristics of the samples were determined by a UV2501-PC Spectrometry (Shimadzu, Japan). The dispersion extent of TiO_2 in PP was observed by a H-800 transmission electron microscope (TEM) (Hitachi, Japan). The rheology of the samples was examined by a PLV-151 Brabender torque rheometer (Brabender, Germany, temperature = 210 °C, rotating speed = 30 rpm).

Fig. 1 shows the TW whiteness index of the composites with a fixed total amount of nano-$CaCO_3$ and TiO_2 added, while TiO_2 is partially replaced by nano-$CaCO_3$ at different doses. It can be seen from Fig. 1 that a partial substitution of nano-$CaCO_3$ for TiO_2 can raise the whiteness of colored PP. The whiteness index of the materials reaches a maximum when 10% of TiO_2 is replaced by nano-$CaCO_3$, which is 4.3% higher than those without any replacements of TiO_2 by nano-$CaCO_3$. This is because nano-$CaCO_3$ can prompt the dispersion of TiO_2 particles in the matrix and boost the coloring effects of the materials. The doses of TiO_2 also reduce accordingly.

Fig. 2 shows the UV absorbency (Abs.) curves of TiO_2 and nano-$CaCO_3$ powders. It can be seen from Fig. 2 that TiO_2 exhibits a very strong absorbency for the UV light in the wavelength of 290–400 nm, while the absorbency of nano-$CaCO_3$ is notably lower than that of TiO_2 in this wavelength range. Fig. 3 shows that UV absorbency curves of colored PP. The UV absorbency of colored PP changes little when TiO_2 is partially replaced by nano-$CaCO_3$. Because nano-$CaCO_3$ can improve the dispersion of TiO_2 in PP matrix, the UV absorptance of TiO_2 remains unchanged even if its concentration is lowered. This result is favorable for the reduction of the product cost while maintaining a good aging resistance performance.

Fig. 4 shows the TEM pictures of PP/TiO_2/$CaCO_3$ composites. Fig. 4a is the TEM picture of PP/TiO_2, without any addition of nano-$CaCO_3$. It is obvious that large aggregates form in this system. Fig. 4b is the TEM picture of PP/TiO_2/$CaCO_3$, while the concentration of TiO_2 keeps unchanged and the dose of nano-$CaCO_3$ accounts for 10% of the dose of TiO_2. Fig. 4c is the TEM picture of PP/TiO_2/$CaCO_3$, while the total concentration of TiO_2 and nano-$CaCO_3$ combined remains

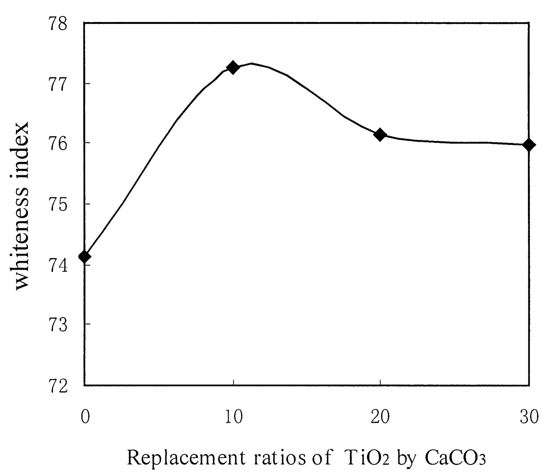

Figure 1 Pigmented PP whiteness for different replacement ratios of TiO_2 by $CaCO_3$.

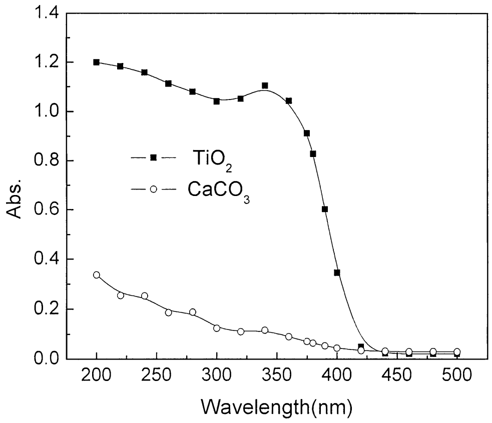

Figure 2 Ultraviolet Abs. of TiO_2 and nano-$CaCO_3$ powders.

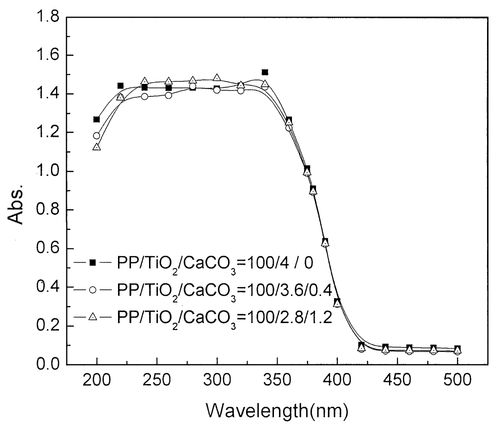

Figure 3 Ultraviolet Abs. of PP/TiO_2/nano-$CaCO_3$ composites.

unchanged and 10% of TiO_2 is replaced by the same amount of nano-$CaCO_3$. By a comparison of Figs. 4a, b and c, it can be seen that the pigment aggregates are dispersed and the small particles become finer in a system with the addition of nano-$CaCO_3$. The uniformity and dispersion of the pigments are also boosted in such a system. These TEM pictures are further verification that nano-$CaCO_3$ can improve significantly the dispersion of particles of pigments in PP matrix. It can be concluded that the performance, especially the whiteness, of the materials can be increased due to the synergism of TiO_2 and nano-$CaCO_3$.

Fig. 5 shows the effect of the addition of nano-$CaCO_3$ on the viscosity of PP composites in the melt state. It can be seen from Fig. 5 that both the maximum torque and equilibrium torque increase in a system with added nano-$CaCO_3$, which indicates that the melt viscosity of system becomes larger. The PP composites with added nano-$CaCO_3$ take a longer time to reach equilibrium, from 4 min to 10 min. A longer processing time is correspondingly required.

The pigment particle size and dispersion are decisive for the coloring effect of plastics. The micronization and dispersion of TiO_2 particles in PP resin depend mainly on the exterior mechanical shear action through the melt-processing. The larger the shear is, the better the dispersion is. During melt-processing the exterior shear is transferred to the dispersive pigment phase via the continuous matrix phase. When the viscosity of the continuous phase increases, the transferred shear increases accordingly. As nano-$CaCO_3$ has very large specific surface area, the surface effect can raise the melt viscosity of the PP composites. Therefore, TiO_2 particles are subjected to a greater shear action and further micronized and dispersed when exterior force acts on the melting blends.

In conclusion, nano-$CaCO_3$ is an excellent pigment dispersant, which can partially replace TiO_2 pigments for PP resin coloring. Nano-$CaCO_3$ can prompt the dispersion of TiO_2 in polymer matrix, boosting the whiteness of the materials without a negative effect on the UV absorbency of the materials.

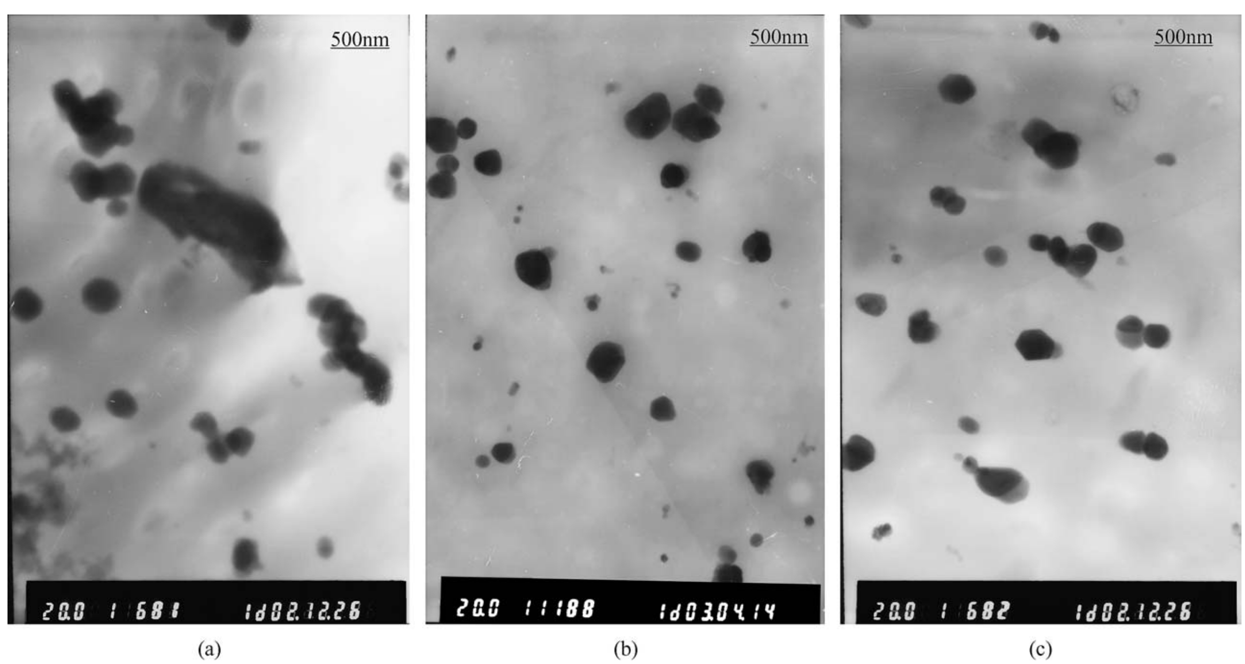

Figure 4 TEM photos of (a) PP/TiO_2/$CaCO_3$ = 100/4/0, (b) PP/TiO_2/$CaCO_3$ = 100/4/ 0.4 and (c) PP/TiO_2/$CaCO_3$ = 100/3.6/0.4.

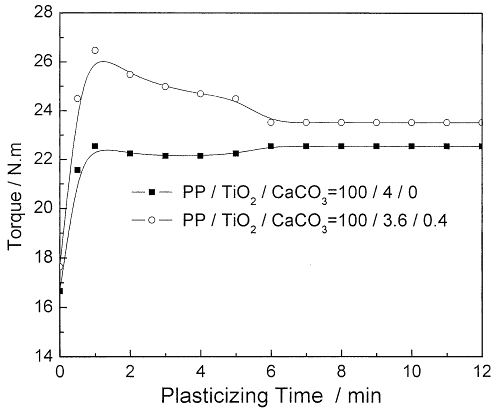

Figure 5 Effect of nano-$CaCO_3$ content on the rheological behavior of PP nanocomposites.

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