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Characterication and control of nanoparticle dispersion behavior for smart processing in liquid phase†

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KEY WORDS: (Nanoparticle) (Aggregation) (Surface treatment) (Dispersion) (Bead milling) (hybrid material) (Organic solvent) (Smart materials) (Powder Technology) (Colloid probe AFM)

1. Introduction

Nanoparticles have already become an indispensable and smart material for many fields of industries because of their unique size dependent properties such as electrical, magnetic, mechanical, optical and chemical properties, which largely differ from those of their bulk materials[1, 2]. Since nanoparticles have different surface structures and surface interactions compared to the sub-micron sized particles, nanoparticles have an extremely high tendency for adhesion and aggregation. Thus, it is quite important to develop techniques to control the dispersion/aggregation phenomena of nano particles to apply them in functional materials and products. In this paper, we focused on the post-synthesis surface modification process for the dispersion of nanoparticles in various organic solvents by using surface chemical reaction of silane coupling agents. In order to redisperse this aggregated dry powder into solvents near to their primary particle size, the mechanical milling method using small beads has recently been developed[3]. The aggregate of dry carbon black nanopartiucles was applied to re-disperse into liquid media by the simultaneous processing of surface modification and the bead milling.

2. Experimental procedure

Surface chemical modification of TiO_2 nanoparticles in aqueous suspension and dispersion behavior in organic solvent

Recently, aqueous colloidal suspensions with well dispersed various kind of inorganic nano particles, such as silica, TiO_2 and ZrO_2, have been marketed by different companies. Since the surfaces of nanoparticles in suspension have a high electric charge and the double layer is formed on surface, nanoparticles were dispersed up to primary particles without aggregation in aqueous media. From commercial TiO_2 aqueous suspension, the surface modification process for dispersion of nano particles in organic solvents is shown in **Fig. 1**[4]. Two kinds of silane coupling agents with different molecular structures and methanol were reacted on the surface of TiO_2 in suspension. If a hydrophobic surface was produced on particles, TiO_2 nanoparticles were precipitate from suspension. In this paper, we investigated mixed silane coupling agents method[5] by using two kinds of agent such as APTMS, NH_2-$(CH_2)_3Si(OCH_3)_3$, (molecular weight : 179.3g/mol, minimum covered surface area : 436 m^2/g), and DTMS, $CH_3(CH_2)_9Si(OCH_3)_3$ (molecular weight : 179.3g/mol , minimum covered surface area : 436 m^2/g). The separated particles were dried and re-dispersed in various organic solvents. The relationship between surface molecular structure and dispersion behavior in organic solvent was discussed by the measurement results of aggregate size distribution. The aggregation behavior in the organic solvent was determined by a dynamic laser scattering method, and surface structure was characterized by FT-IR. The amount of surface modified silane coupling agent was determined by TG-DTA and CHN analyzer after washing of free silane coupling agent.

Dispersion of carbon black suspension by agitation milling used small beads of 30 μm in diameter and simultaneous processing of surface modification

Carbon black particles (specific surface area : 225 m^2/g) was dispersed into N-metyl-2-pyrrolidone, NMP, with maleic acid anhydride, for which surface area based concentration was fixed at 17.0 μmol/m^2. The aggregates in suspension were dispersed by an agitation bead mill. The effects of agitation milling time on aggregate size distribution were determined by laser scattering method. After milling, surface treated carbon black was washed and dried. Finally, surface modified carbon black particles were reacted with NaOH in aqueous solution or epoxy and tetra-butyl-ammoniun-bromide, TBAB, toluene solution at 363 K for 24 h. After drying of each surface treated carbon black particles, the amount of surface reacted molecules were determined by TG-DTA, and dispersion behavior of each treated particle was observed in water with pH adjusted at 11 and toluene.

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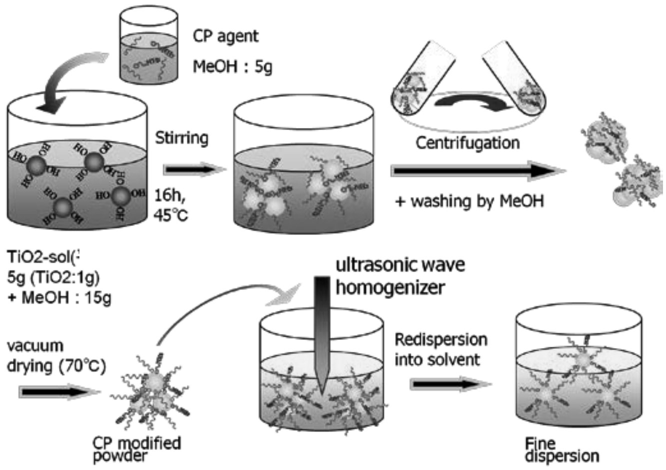

Fig. 1 Preparing process of surface modified TiO_2 particles

3. Results and discussion

Dispersion behavior of surface treated TiO_2 nano particle with different silane coupling agents in various organic solvents

Surface molecular structure of TiO_2 nanoparticles was characterized by FT-IR and the functional group of each coupling agent was confirmed. By using the surface treatment process as shown in Fig. 1, it is possible to modify and produce hydrophobic chain on TiO_2 nanoparticles. The dispersion behavior of surface modified particles with different conditions was observed in different organic solvents. Based on the observation and aggregate size distribution determined by dynamic laser scattering method, an example of the dispersion map was shown in **Fig. 2**. This figure shows the dispersion behavior of TiO_2 nanoparticles with different reacted amounts of APTMS and DTMS, in various organic solvents. The amount of reacted silane coupling agent was controlled by the additive content of each silane coupling agent and determined by CHN analysis. If a transparent suspension was obtained and the mean aggregate size was smaller than 100 nm, we decided that the surface modified particle was dispersible in each organic solvent. The optimum surface modified amount of each silane coupling agent in various organic solvents was determined by using this map.

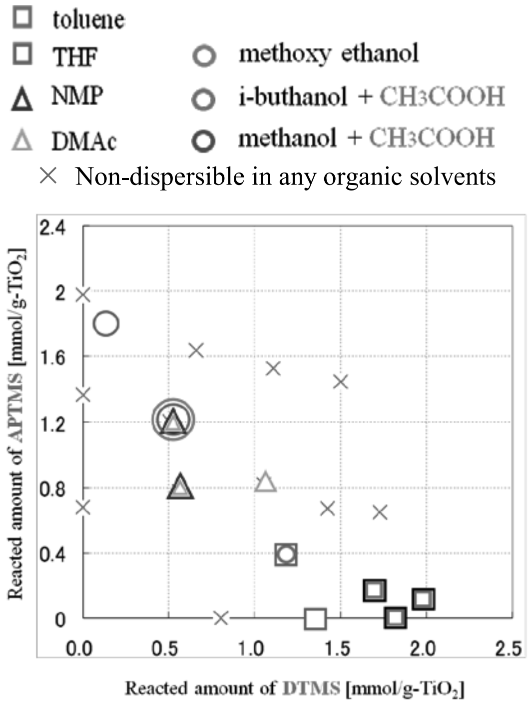

Fig. 2 Dispersion behavior of surface treated TiO_2 nanoparticles with different amounts of reacted silane coupling agent in various organic solvents

Dispersion of carbon black suspension by agitation milling used small beads of 30 μm in diameter and simultaneous processing of surface modification

The effect of milling time on size distribution is shown in **Fig. 3**. The minimum aggregate size was observed at 2 hr milling time. The longer milling time caused an increase in the aggregate size.

The dispersion behavior of carbon black nanoparticles with different surface modification conditions in water (pH = 11) and toluene was observed and shown in **Fig. 4**. If a hydrophilic functional group was produced on carbon black, carbon was able to disperse in water. When an epoxy group was produced on the carbon surface, carbon black was able to disperse in water and toluene. The multiple surface treatment of carbon was useful for the dispersion in polar and non-polar solvents.

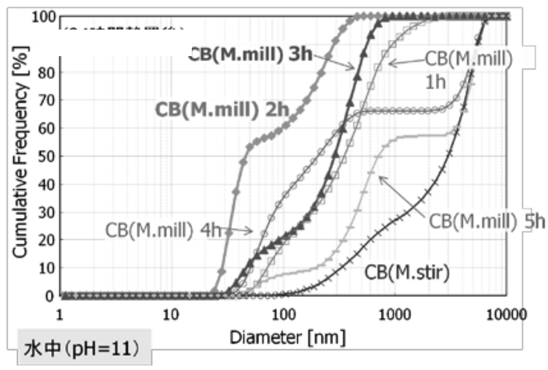

Fig. 3 Effect of milling time on aggregate size distribution in aqueous suspension

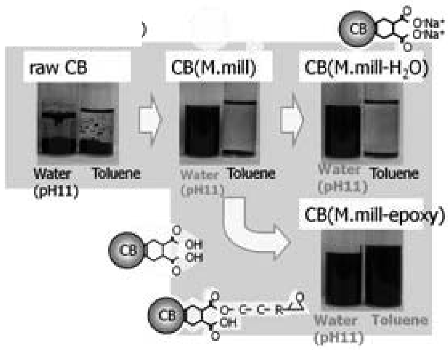

Fig. 4 Dispersion behavior of surface treated carbon black particles with different conditions in water and toluene

4. Conclusions

Dispersion behavior of TiO_2 and carbon black nanoparticles was able to be controlled by the surface modification and physical bead milling method in organic solvent and water.

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