Bull. Chem. Soc. Jpn., 57, 2659—2660 (1984)

Zeta Potentials of Metal Oxides in Aqueous Solution of Water-soluble Titanate Coupling Agents

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(Received January 13, 1984)

Synopsis. The zeta potentials of γ-Fe_3O_4 and TiO_2 were measured as a function of the amount of water-soluble titanate coupling agents added in aqueous solution. Compared with untreated samples, the zeta potential of γ-Fe_3O_4 increased negatively with an increase of the amount of water-soluble titanate coupling agents, while that of TiO_2 changed little. Furthermore, after a washing process, it was confirmed by ESCA measurement that a certain amount of water-soluble titanate coupling agent still remained on the surface of the γ-Fe_3O_4.

Silane and titanate coupling agents for modifying many fillers have been employed[1-3] to improve the bonding between reinforcements and polymer matrices. When coupling treatments are applied to a dispersion system containing porous material in solution, electrokinetic measurement[4] is a useful method to detect changes in the surface properties. Esumi *et al.*[5,6] studied the change in the zeta potential of metal oxides coated with coupling agents and they found that the zero point of the charge of the metal oxides coated with (3-aminopropyl)triethoxysilane and tris[2-(2-aminoethylamino)ethoxy]isopropoxytitanium(IV) is shifted to a higher value.

It is known that chelated titanate coupling agents can be made water-soluble *via* a quaternization technique which converts water-insoluble chelated titanates to water-soluble, ionic quadrivalent nitrogen salt complexes. Such water-soluble titanate coupling agents seem very interesting materials because they can be applied to aqueous dispersion system.

In this work the influence of water-soluble titanate coupling agents on the surface properties of γ-Fe_3O_4 and TiO_2 was investigated by measuring their zeta potential and ESCA spectra.

Experimental

Materials. The titanate coupling agents used in this study were bis{*O′*,*O′*-dioctyl pyrophosphato(1-)}(1-oxoethylenedioxy)titanium(KR-238S) and bis{*O′*,*O′*-dioctyl pyrophosphato(1-)}(ethylenedioxy)titanium(KR-138S), kindly supplied by Ajinomoto Co. As metal oxides, γ-Fe_3O_4 and TiO_2 (rutile) were obtained from BASF and Teikoku Kako, respectively. The specific surface areas of γ-Fe_3O_4 and TiO_2 determined by nitrogen adsorption at its liquid temperature were 6.1 and 49 m^2/g. The zero point of charge for sample was 7.5 for γ-Fe_3O_4, 4.2 for TiO_2.

Procedure. Quaternization of titanate coupling agents was made by the addition of triethylamine(TEA) into the coupling agents. The mixing ratios were 1:1 bg weight for KR-138S-TEA and 1:0.5 for KR-238S-TEA. The water-soluble titanate coupling agent obtained was then added to deionized water and the metal oxide added to the solution, dispersed in an ultrasonic cleaning bath.

Measurements of the zeta potential for the dispersed system were conducted using a Pen Kem Laser 500 Zeta Potential. The pH of the suspension was measured with a Corning pH meter.

ESCA spectra of γ-Fe_3O_4 treated with water-soluble titanate coupling agents were obtained using a Kokusaidenki VK-5B photoelectron spectrometer equipped with an aluminium *Kα* X-ray source.

Results and Discussion

Figure 1 shows the zeta potentials of γ-Fe_3O_4 and the pH values of the suspensions as a function of the amount of water-soluble titanate coupling agents added. The zeta potential value of γ-Fe_3O_4 increased negatively with increase of the amount of KR-238S-TEA added and reached about −40 mV, while the pH of the suspension was in the range between 7—7.8. Since

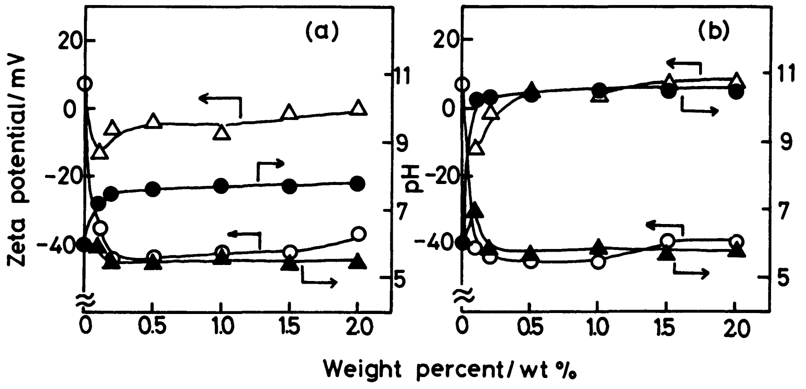

Fig. 1. Zeta potential of γ-Fe_3O_4 and the pH value of the suspension as a function of amount added of water-soluble titanate coupling agents: (a) KR-238S-TEA, (b) KR-138S-TEA; (○,●) immediate measurement, (△,▲) measurement after washing process.

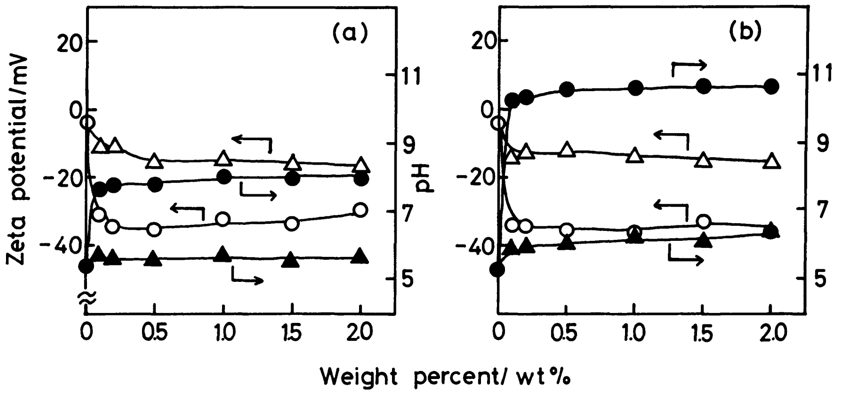

Fig. 2. Zeta potential of TiO_2 and the pH value of the suspension as a function of amount added of water-soluble titanate coupling agents: (a) KR-238S-TEA, (b) KR-138S-TEA, (○,●) immediate measurement, (△,▲) measurement after washing process.

the zero point of the charge (ZPC) for untreated γ-Fe_3O_4 was about 7.5, it seems that the complexes of KR-238S-TEA are adsorbed on the surface of γ-Fe_3O_4, resulting in a negative zeta potential. The change in the zeta potential of γ-Fe_3O_4 by addition of KR-138S-TEA was analogous to that for KR-238S-TEA. Further, from the measurement of the ESCA spectra for the samples treated with KR-238S-TEA and KR-138S-TEA, a Ti 2P photopeak due to water-soluble titanate coupling agents was detected. This result indicates that these water-soluble titanate coupling agents are adsorbed on γ-Fe_3O_4.

The attachment strength of the water-soluble titanate coupling agents was estimated by measuring the zeta potential of γ-Fe_3O_4 treated after a washing process. The γ-Fe_3O_4 particles in the presence of the water-soluble titanate coupling agent were collected and washed five times with a 10 ml of deionized water, then dispersed in deionized water. After such a washing process, the zeta potential of γ-Fe_3O_4 for KR-238S-TEA showed a negative value, while the sample for KR-138S-TEA provided a positive zeta potential with a value of +12 mV which is almost the same as for the untreated sample at pH=5.5. These results suggest that after washing, for KR-238S-TEA some titanate molecules still remain on the surface of γ-Fe_3O_4, but not for KR-138S-TEA. To confirm that some titanate molecules exist on the surface of γ-Fe_3O_4 after the washing process, ESCA spectra were measured. It was observed that the Ti 2P photopeak for KR-238S-TEA was detected, but not for KR-138S-TEA. Thus, it is found that the attachment of KR-238S-TEA on the surface of γ-Fe_3O_4 is much stronger than that of KR-138S-TEA.

Figure 2 gives the zeta potential of TiO_2 and the pH of the suspension for addition of various amounts of water-soluble titanate coupling agents. In both KR-138S-TEA and KR-238S-TEA, the zeta potential values by addition of the water-soluble titanate coupling agents were close to those of the untreated samples, indicating that adsorption of these titanate coupling agents scarcely occurs on TiO_2 or may occur by ion exchange. Also, after the washing process, the zeta potential of TiO_2 was −20 mV which is almost identical to that of the untreated sample at about pH=6. Thus, the zeta potential of TiO_2 by addition of various amounts of water-soluble titanate coupling agents and after the washing process changed little compared with that of an untreated sample.

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