Zeta Potentials of Metal Oxides Coated with Titanate Coupling Agents in Aqueous Solution

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Synopsis. The zeta potentials of metal oxide surfaces coated with titanate coupling agents were measured as a function of pH in the suspensions. The treatment by titanium(IV) isopropoxide tris(2-methylheptadecanoate) on the metal oxides, such as iron oxide, titanium dioxide, and silica, provided lower zeta potential values over a wide pH range than those of untreated samples. On the other hand, the treatment of the samples by titanium(IV) tris[2-(2-aminoethylamino)ethoxide] isopropoxide rendered the surfaces more cationic. Further, it was found that the titanate coupling layer was almost removed from the surfaces after one day they were immersed in aqueous solution.

Silane coupling agents[1,2] for modifying many fillers have been used to improve the bonding between reinforcements and polymer matrix. Recently, as coupling agents, titanate coupling agents[3] have been attractive for chemical bridges between the interface of an inorganic substrate and the polymer. It is believed that titanate coupling agents form a monomolecular layer on the inorganic substrate providing polymer compatibility and a reduction in the water of hydration and air voids in the inorganic substrate. Accordingly, it seems important to elucidate the interaction between the surface of inorganic substrate treated with titanate coupling agents and aqueous solution.

For this purpose, in this work, the zeta potentials of inorganic substrates treated with titanate coupling agents were measured as a function of pH in aqueous solution.

Experimental

Materials. Two titanate coupling agents, such as titanium(IV) isopropoxide tris(2-methylheptadecanoate) and titanium(IV) tris[2-(2-aminoethylamino)ethoxide] isopropoxide, were kindly supplied by Ajinomoto Co., and were used without further purification. Metal oxides employed were titanium dioxide(rutile type), iron oxide, and silica supplied by Teikoku Chemicals, Titan Chemicals, and Nippon Aerosil Co, respectively.

Procedure. Coating of titanate coupling agents on metal oxide surfaces was carried out with about 3 wt% solution of titanate coupling agents in an organic solvent. For titanium(IV) isopropoxide tris(2-methylheptadecanoate), hexane was used as a solvent and 2-propanol for titanium(IV) tris[2-(2-aminoethylamino)ethoxide] isopropoxide. Then, the metal oxide was added and stirred into the titanate coupling agent solution for 20 min at room temperature. The metal oxide coated with the titanate coupling agent was collected and dried in an oven at 80 °C for 20 min.

Measurements of zeta potential for the metal oxides before and after their titanate coupling agent treatments were made using a Pen Kem Laser 500 Zeta Potential. The pH of the suspension was adjusted with HCl or NaOH.

Results and Discussion

When metal oxides are treated with titanate coupling agents consisting hydrophilic and hydrophobic groups, it is considered that the hydrophilic group of the coupling agent is oriented to the surface of metal oxide and as a result, the treated surface shows hydrophobicity due to exposure of hydrophobic group to outward.

The stability of untreated and titanate coupling agent treated metal oxide suspensions was compared visually in small beakers. The untreated metal oxides were readily dispersible in aqueous solution by gentle shaking, while the treated metal oxides were initially aggregated and floated on the surface of water. However, they dispersed when the suspensions were treated in an ultrasonic cleaning bath.

Figure 1 depicts zeta potentials of untreated and

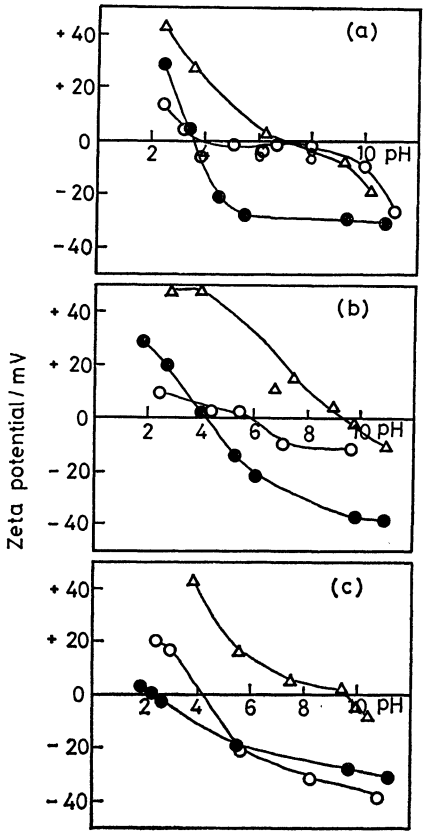

Fig. 1. Zeta potentials of untreated and titanate coupling agents treated metal oxides as a function of pH in suspensions: (a) iron oxide, (b) titanium dioxide (rutile type), (c) silica; (●) untreated, (○) titanium(IV) isopropoxide tris(2-methylheptadecanoate), (△) titanium(IV) tris[2-(2-aminoethylamino)ethoxide]isopropoxide.

titanate coupling agents treated metal oxides as a function of pH in aqueous suspensions. It can be seen from Fig. 1 that the magnitude of zeta potentials for iron oxide and titanium dioxide treated with titanium-(IV) isopropoxide tris(2-methylheptadecanoate) was smaller in a pH range from 2 to 12 than that of untreated samples. In case of silica, the zeta potential treated with titanium(IV) isopropoxide tris(2-methylheptadecanoate) showed a similar behavior as a function of pH to that of untreated samples. This result may suggest that titanium(IV) isopropoxide tris(2-methylheptadecanoate) does not provide a strong coating on the surface of silica. On the other hand, the zeta potentials of all the samples treated with titanium-(IV) tris[2-(2-aminoethylamino)ethoxide] isopropoxide were much positively over a wide pH range than those of untreated samples. As a result, the zero point of charge (ZPC) of their treated samples shifted to much higher values. Similar behavior has been observed[4] in change of the zeta potential of metal oxides treated with aminosilane coupling agents.

It is also important to study the stability of deposited titanate coupling agent layers on the metal oxides in aqueous solution. For this purpose, the samples treated with two kinds of titanate coupling agents were allowed to stand for one day in aqueous solution at a some pH value and then the zeta potential was measured. The results are given in Fig. 2. The zeta potentials of metal oxides treated with the titanate coupling agents in the suspensions after one day became near the value of the untreated metal oxides as a function of pH in the suspensions. These results indicate that the titanate coupling agent layer was almost removed from the metal oxide surface after one day it was immersed in aqueous solution. Thus, it is suggested that the attachment of titanate coupling agent layer on the surface of metal oxide is not strong in aqueous solution. On the other hand, it has been reported[4] that the zeta potentials of iron oxide, titanium dioxide(rutile type), and silica treated with aminosilane coupling agents were not significantly changed even after one day storage in aqueous solution at a some pH value.

Thus, zeta potential measurement is a useful method to elucidate surface properties of metal oxides treated with titanate coupling agents.

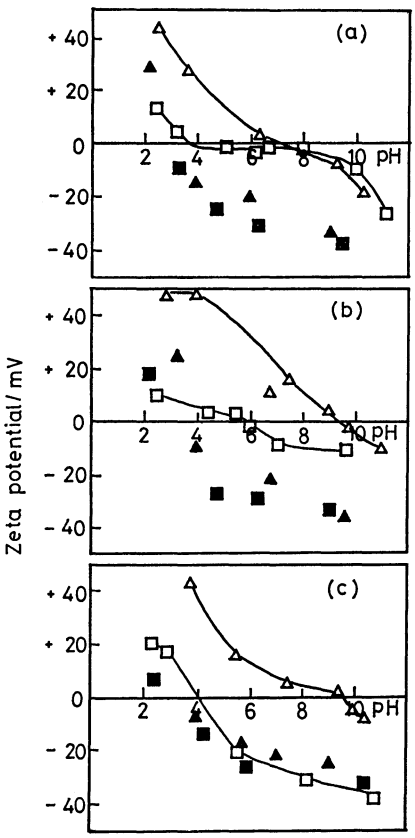

Fig. 2. Effect of storage on zeta potential of metal oxides treated with titanate coupling agents as a function of pH in suspensions: (a) iron oxide, (b) titanium dioxide(rutile type), (c) silica; (□) titanium(IV) isopropoxide tris(2-methylheptadecanoate), (△) titanium(IV) tris[2-(2-aminoethylamino)ethoxide]isopropoxide. Open mark refers to immediate measurement and closed mark to measurement after one day.

References

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