

PREPARATION AND APPLICATIONS OF NOVEL FLUOROALKYL END-CAPPED OLIGOMERS/TITANIUM OXIDE NANOCOMPOSITES

Eri Sawada^a, Hiroshi Kakehi^{b,c}, Yukiyasu Chounan^b, Masashi Miura^c, Yusuke Sato^c, Norifumi Isu^c, and Hideo Sawada^{b*}

^aGraduate School of Education, Hirosaki University, Bunkyo-cho, Hirosaki 036-8560, Japan

^bGraduate School of Science and Technology, Hirosaki University, Bunkyo-cho, Hirosaki 036-8561, Japan

^cR & D Center, INAX Corporation, Tokoname, Aichi 479-8588, Japan

*E-mail address: hideosaw@cc.hirosaki-u.ac.jp

Introduction

The sol-gel method with titanium alkoxides is very popular technology for the preparation of organic polymers/titanium oxide nanocomposites; however the exploration of organic polymers/titanium oxide nanocomposites by the direct use of titanium oxide nanoparticles have been hitherto very limited because of their poor dispersibility in a variety of solvents, although the development of these nanocomposites should be deeply desirable from the practical point of view.[1] During our comprehensive studies on the preparation of fluorinated polymers/transition-metal oxide or metal nanocomposites possessing good dispersibility and stability in a variety of solvents [2], we have found that fluoroalkyl end-capped vinyltrimethoxysilane oligomer is a convenient tool for the preparation of the expected fluorinated polymer/titanium oxide nanocomposites. In addition, these nanocomposites were applied to the surface modification of glass to exhibit not only a completely superhydrophobic characteristic (a water contact angle: 180°) with a non-wetting property against water droplets but also a good oleophobicity on their surface. Interestingly, the wettability for water can be switched between superhydrophobicity and superhydrophilicity by alternation of ultraviolet (UV) irradiation and dark storage with a good oleophobicity. These results will be described herein.

Experimental

Materials

Titanium oxide nanoparticles (size of anatase-type particle: 20 nm; size of rutile-type particle: 35 nm) were received from Ishihara Sangyo Kaisha Ltd. (Osaka, Japan). Fluoroalkyl end-capped vinyltrimethoxysilane oligomer was prepared by reaction of fluoroalkanoxy peroxide with the corresponding monomer according to our previously reported method.[3]

Preparation of fluoroalkyl end-capped vinyltrimethoxysilane oligomer/titanium oxide nanocomposites

A typical procedure for the preparation of fluorinated oligomer/titanium oxide nanocomposites is as follows: to a tetrahydrofuran (THF) solution (20 ml) of fluoroalkyl end-capped vinyltrimethoxysilane oligomer: R_F-(VM)_n-R_F; R_F = CF(CF₃)OC₃F₇; Mn = 1030, 400 mg] were added anatase-type TiO₂ nanoparticles (500 mg) and 25 % aqueous ammonia solution (0.25 ml). The mixture was stirred with a magnetic stirring bar at room temperature for 2 hr, and then was centrifuged for 30 min. The expected fluorinated TiO₂ nanocomposites were easily separated from the THF solution. THF (20 ml)

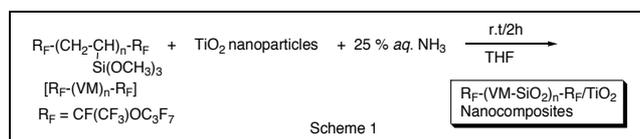
was added to the obtained crude product. The THF solution was stirred with magnetic stirring bar at room temperature for 1 day. After centrifugal separation of this solution, the obtained product was dried in vacuum at 50 °C for 2 days to produce purified fluorinated composite white colored powders (531 mg).

Surface modification of glass with fluoroalkyl end-capped vinyltrimethoxysilane oligomer/titanium oxide nanocomposites

The THF solution (20 ml) containing R_F-(VM)_n-R_F oligomer [R_F = CF(CF₃)OC₃F₇: 500 mg], anatase-type titanium oxide nanoparticles (500 mg) and 25 % aqueous ammonia solution (0.25 ml) was stirred with a magnetic stirring bar at room temperature for 1 hr. The glass plate (18 x 18 mm² pieces) was dipped into this THF solution at room temperature and left for 5 min. This was lifted from the solution at a constant rate of 0.5 mm/min, and subjected to the treatment for 1 day at room temperature after washing with water, and finally dried in vacuo for 1 day at room temperature. After drying, the contact angles of water and dodecane for this glass plate were measured.

Results and discussion

Fluoroalkyl end-capped vinyltrimethoxysilane oligomer [R_F-(VM)_n-R_F] suffered the sol-gel reaction under alkaline conditions in the presence of anatase-type titanium oxide nanoparticles in tetrahydrofuran (THF) to afford the corresponding fluorinated oligomer/TiO₂ nanocomposites [R_F-(VM-SiO₂)_n-R_F/TiO₂] in excellent to moderate isolated yields. Similarly, we succeeded in preparing fluorinated rutile-type nanocomposites in 55 ~ 62 % isolated yields. These results were shown in Scheme 1 and Table 1



R_F-(VM-SiO₂)_n-R_F/TiO₂ nanocomposites in Table 1 exhibit no dispersibility in water; however, it was demonstrated that these composites can exhibit good dispersibility and stability in traditional organic solvents such as 1,2-dichloroethane, THF, methanol, ethanol, and isopropyl alcohol, ethyl acetate, acetone, and fluorinated aliphatic solvents (AK-225: 1 : 1 mixed solvents of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane). Thus, we have measured the size of R_F-(VM-SiO₂)_n-R_F/TiO₂ composites in methanol by dynamic light-scattering

(DLS) measurements at 25 °C. These results were also shown in Table 1.

Run	$R_F-(VM)_n-R_F$ (mg)	TiO_2 nanoparticle (mg)	25w% aq. NH_3 (ml)	Yield ^{a)} (%)	Particle Size \pm STD (nm)	Content of oligomer in composites ^{c)} (%)
1	400	500*	0.25	59	12.1 \pm 3.4	39
2	400	500**	0.25	62	20.7 \pm 5.8	44
3	400	250*	0.25	50	246.8 \pm 56.3	54
4	400	250**	0.25	55	231.5 \pm 54.5	58

a) Yield based on $R_F-(VM)_n-R_F$ and TiO_2
b) Size of redispersed nanocomposites in MeOH by DLS
c) Determined by thermogravimetric analyses measurements
*) Anatase-type TiO_2 nanoparticles
**) Rutile-type TiO_2 nanoparticles

As shown in Table 1, each size of these obtained fluorinated TiO_2 composites is nanometer size-controlled fine particles (12 ~ 247 nm: number-average diameter). In particular, the size of the composites was found to decrease with the increase of the feed amounts of anatase- or rutile-type TiO_2 nanoparticles from 250 to 500 mg, indicating that TiO_2 should be more effectively encapsulated into the cross-linked fluoroalkyl end-capped vinyltrimethoxysilane oligomeric matrix cores to afford more fine nanocomposite particles.

In order to clarify the presence of TiO_2 in the composites, we have analyzed these nanocomposites by the use of thermogravimetric analyses (TGA), in which the weight loss of these nanocomposites was measured by raising the temperature around 800 °C (the heating rate: 10 °C/min) in air atmosphere, and the results were shown in Fig. 1.

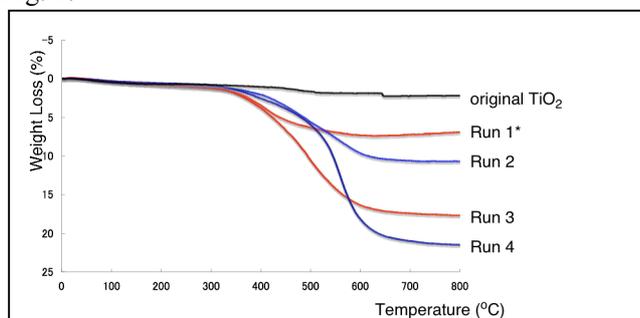


Fig. 1 Thermogravimetric analyses of original TiO_2 and $R_F-(VM-SiO_2)_n-R_F/TiO_2$ nanocomposites

*) Each different from those of Table 1

Parent $R_F-(VM-SiO_2)_n-R_F$ composite, which was prepared by the sol-gel reaction of the corresponding oligomer under similar conditions as that of Scheme 1, decomposed at 800 °C to exhibit the 67 % weight loss behavior due to the partly formation of silica gel during the calcination process (data not shown). On the other hand, $R_F-(VM-SiO_2)_n-R_F/TiO_2$ nanocomposites were found to decompose significantly compared to that of the parent TiO_2 during the calcination process from room temperature to 800 °C. The contents of fluorinated oligomer in the nanocomposites were estimated to be 39 ~ 54 % (see Fig. 1) based on the weight loss of TiO_2 and parent $R_F-(VM-SiO_2)_n-R_F$ composite.

Our present $R_F-(VM-SiO_2)_n-R_F/TiO_2$ nanocomposites are strongly expected to exhibit photoinduced hydrophilicity

with keeping a good oleophobicity imparted by fluorine. Thus, we tried to apply our present fluorinated titanium oxide nanocomposites to the surface modification of glass. We have prepared the modified glass treated with $R_F-(VM-SiO_2)_n-R_F/TiO_2$ nanocomposites, and the contact angles of dodecane and water on the modified glasses were measured. The contact angle of dodecane on the modified glass surface significantly large value: 42°, which exhibits a good oleophobicity imparted by fluoroalkyl segments in nanocomposites on the modified glass surface, compared to that (0°) of the nontreated glass. On the other hand, we have observed a completely superhydrophobic coating surface, which exhibits a water contact angle of 180° on the modified glass surface. This finding would be due to the fabrication of appropriate surface roughness with hydrophobic fluoroalkyl segments in the composites. In contrast, interestingly, upon UV irradiation (λ_{max} : 356 nm) for 50 min, the water droplet was found to spread out on the modified glass surface, resulting in the decrease of contact angles of water from 180° to 105°. More interestingly, a steep time dependence of contact angle values for water was observed in the modified glass surface. The contact angles were found to decrease from 108° to 0° over 30 min, although the contact angle of dodecane on the modified glass surface was found to afford the constant value: 42° under similar conditions.

Conclusion

We have succeeded in preparing novel $R_F-(VM-SiO_2)_n-R_F/TiO_2$ nanocomposites by the sol-gel reaction of fluoroalkyl end-capped vinyltrimethoxysilane oligomer in the presence of titanium oxide nanoparticles under alkaline conditions. DLS measurements show that these composites are nanometer size-controlled fine particles. These fluorinated nanocomposites were found to exhibit good dispersibility and stability in traditional organic solvents except for water. These fluorinated nanocomposites were also applied to the surface modification of glass, and the modified glass surface was found to exhibit a good oleophobicity imparted by fluoroalkyl segments. More interestingly, this modified glass surface was able to exhibit a switching behavior between superhydrophobicity and superhydrophilicity by the UV irradiation with a good oleophobicity imparted by fluorine.

Acknowledgement

This work was partially supported by a grant-in-aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

References

- [1] W.-C. Chen, S.-J. Lee, L.-H. Lee, and J.-L. Lin, *J. Mater. Chem.*, **9**, 2999 (1999);
- [2] a) H. Sawada, *Prog. Polym. Sci.*, **32**, 509 (2007);
b) H. Sawada, *Polym. J.*, **39**, 637 (2007).
- [3] H. Sawada and M. Nakayama, *J. Chem. Soc., Chem. Commun.*, 677 (1991).