Surface Modification of Titania Particles with Urushiol (Japanese Lacquer) and Its Application to the Preparation of Polymer–Titania Hybrids

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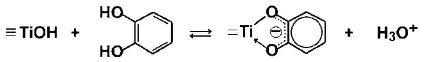
To prepare stable polymer–titania hybrids, titania particles were modified using urushiol (extracted from Japanese lacquer) via surface complexation. The urushiol moieties underwent hydrosilylation and radical graft-polymerization to yield polymer–titania hybrids in which the titania particles were dispersed in polymer matrices.

Polymer-based hybrids that include inorganic components have been attracting considerable interest, since inorganic components have the potential to add various properties to polymers. The dispersion of crystalline metal oxide particles into polymer matrices is one of the common approaches, moreover, since this can improve the polymers' thermal, mechanical, and electrical properties.[1] These polymer–metal oxide hybrids can be prepared by dispersion of particles into melted polymers or by polymerization of monomers in the presence of particles. Upon dispersion, however, phase separation due to a weak interaction between the inorganic particles and the polymer network generally occurs.[2]

To achieve stable hybrids, the metal oxide particles should be stabilized in the polymer matrix with strong bonds such as covalent bonds. Formation of strong bonds between the organic moieties and metal oxide particles to immobilize the particles in the polymer matrices is consequently extremely important. Surface modification of metal oxide particles with organic moieties has typically been achieved by means of reactions between the surface hydroxy groups of metal oxide particles (M–OH) and coupling reagents such as organosilane[3,4] and organophosphorus compounds.[5] This process, called a "grafting reaction," is essential for the modification of metal oxide particles, and high dispersibility of the metal oxide–polymer hybrids can be expected.[3]

On the other hand, the surface hydroxy groups possess the potential to form surface complexes with a wide variety of organic or inorganic compounds. This reactivity can be utilized to bind organic moieties onto metal oxide particles. Surface complexation has been investigated mainly in connection with systems containing titania particles and benzene-derivative ligands, especially systems containing chelate ligands such as catechol ($C_6H_4(OH)_2$). Surface modification with catechol can be described as chemisorption (Scheme 1) due to the replacement of the surface hydroxy groups with a deprotonated ligand ($C_6H_4O_2{}^{2-}$).[6]

The dispersion of nonsilica particles, such as titania particles, has been expected to provide better reinforcement,[7] and polymer–titania hybrids have so far been mainly obtained as mixtures of polymers and amorphous titana through the use of titanium alkoxides.[8] Some hybrids that include crystalline titania particles introduced through surface modification with dopamine (a catechol derivative) have, however, been reported recently.[9] Surface complexation can thus be regarded as a versatile surface modification that can bind various organic moieties onto crystalline titania particles and that can be utilized for the preparation of polymer–titania hybrids.

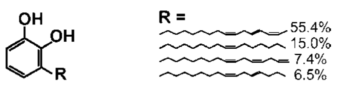


Scheme 1. Surface complexation of titania particles and catechol.

Here, we report a novel preparation of polymer–titania hybrids via surface complexation. The organic modification onto titania particles was performed with urushiol (a main component of Japanese lacquer), in which catechol moieties can react with titania particles through surface complexation and whose alkenyl groups also exhibit reactivity (Scheme 2). In order to form polymer matrices, hydrosilylation with hydride-terminated polydimethylsiloxane (H-PDMS; $HSi(CH_3)_2O[Si(CH_3)_2O]_n$-$(CH_3)_2SiH$) and graft-polymerization[4] using methyl methacrylate (MMA; $C_2H_2(CH_3)COOCH_3$) were conducted on the urushiol moieties bound onto the titania particles.

The surface complexation of titania particles was conducted using P-25 (Degussa Corp., surface area: $50\,m^2{\cdot}g^{-1}$) with urushiol[10] (extracted from the sap of urushi[11]). Urushiol was added into a suspension of titania particles in water, immediately turning the suspension to a pale red color. The suspension was then stirred with a magnetic stirrer for two days. The resultant suspension was centrifuged, washed with ethanol and petroleum ether, and dried under reduced pressure, and a pale red powdery product ([TiO_2–uru]) was obtained. The diffuse reflectance UV–vis spectrum of [TiO_2–uru] (Figure 1b) exhibits a broad peak ($\leq$700 nm) centered at 420 nm, in addition to a fundamental absorption peak due to crystalline titania ($\leq$380 nm). Since a very similar peak centered at 420 nm was reported for the titania–catecholate surface complex,[7] the observed peak can be assigned to a ligand-to-metal charge-transfer transition, suggesting the formation of a surface complex from titania and urushiol.

The diffuse reflectance infrared (IR) spectrum of [TiO_2–uru] exhibited absorption bands due to urushiol moieties such as ν(CH) (3015, 2930, and 2850 cm^{-1}), δ(CH) (1450 cm^{-1}), and ν(CO) (1280 and 1190 cm^{-1}).[12] A solid-state ^{13}C nuclear magnetic resonance spectrum with cross polarization and magic angle spinning techniques (CP/MAS NMR) of [TiO_2–uru] also showed signals due to CH_3 groups (17 ppm), CH_2 groups



Scheme 2. Components of urushiol.[10]

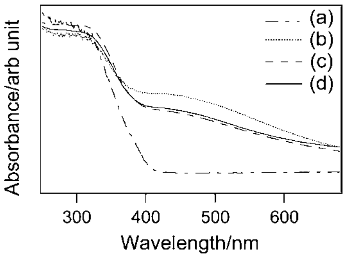


Figure 1. Diffuse reflectance UV–vis spectra of (a) TiO_2 particles, (b) [TiO_2–uru], (c) PDMS–titania hybrid, and (d) PMMA–titania hybrid.

(30 ppm), and C=C groups and aromatic groups (110–140 ppm). In addition, a new broad signal was observed at around 155 ppm that exhibited a considerable downfield shift from the chemical shift of the C–OH carbon in urushiol (142 and 143 ppm). The downfield shift of the C–OH signal appears to indicate the coordination of catecholate moieties to titanium surface sites as a deprotonated form, since a very similar downfield shift (from 144 to 155, 157 ppm) was observed upon the reaction of titanium *tert*-butoxide [$Ti(OC(CH_3)_3)_4$] with catechol to form [$Ti(cat)(OC(CH_3)_3)_2$].[13] It can, therefore, be concluded that surface complexes are formed between titania and deprotonated forms of urushiol. The amount of urushiol moieties on the titania particles was estimated to be 1.3 ($\pm$0.1) $\times 10^{-4}$ mol·g^{-1}, based on the carbon content of [TiO_2–uru], 3.1 ($\pm$0.2) mass %.

In order to obtain a polymer–titania hybrid, we conducted hydrosilylation between [TiO_2–uru] and H-PDMS with a short chain ($n = 6$) in the presence of Karstedt's catalyst ($O[Si(CH_3)_2CH{=}CH]_2Pt$) at 60 °C for 1 d, and a powdery product was obtained. The IR (diffuse reflectance) and ^{29}Si CP/MAS NMR spectra of the product exhibited the presence of a siloxane chain. The disappearance of the ν(SiH) absorption band (2130 cm^{-1}; H-PDMS), moreover, and a decrease in the intensity of the $\nu(\mathrm{C{=}\underline{CH}})$ (3015 cm^{-1}; [TiO_2–uru]) absorption band were observed. Correspondingly, the ^{29}Si CP/MAS NMR spectrum of the product exhibited the appearance of a signal assigned to the CH_2–$Si(CH_3)_2O$– environment (6–9 ppm) and the lack of a signal due to the $HSi(CH_3)_2O$– environment (-7.0 ppm; H-PDMS). These results indicate successful hydrosilylation between the C=C groups in the urushiol moieties on titania particles and the Si–H groups of H-PDMS. Transmission electron microscopy (TEM) images of the product (not shown), however, exhibited the aggregation of titania particles. H-PDMS with a longer siloxane chain ($n \approx 230$) was consequently employed for hydrosilylation, and a geled product was obtained. A TEM image of the geled product shows that titania particles (black dots) are dispersed in the polymer matrix (Figure 2a).

Radical graft–polymerization between [TiO_2–uru] and MMA (distilled under reduced pressure) was performed with various amounts of MMA in the presence of 2,2′-azobisisobutyronitrile (AIBN) at 60 °C for 1 d, leading to the formation of powdery products (urushiol/MMA $\geq 1/10$) and a rubber-like product (urushiol/MMA $= 1/50$). In the IR (diffuse reflectance) spectra of the powdery products, the relative intensities of the $\nu(\mathrm{C{=}\underline{CH}})$ absorption bands due to both [TiO_2–uru] (3010 cm^{-1}) and MMA (3107 cm^{-1}), in comparison with the band area of the ν(CH) band of the CH_3 group in MMA (2955 cm^{-1}) and the bands of the CH_2 chain (2925 cm^{-1}) in [TiO_2–uru], showed remarkable decreases,[12] indicating that the polymerization involved the C=C groups of both MMA and [TiO_2–uru]. The amount of MMA was insufficient, however, to form a PMMA–titania hybrid possessing dispersed titania particles. The rubber-like product, on the other hand, whose IR spectrum was very close to that of PMMA, possessed titania particles dispersed in a PMMA matrix. A typical TEM image is shown in Figure 2b, and every part of the products had a similar microstructure.

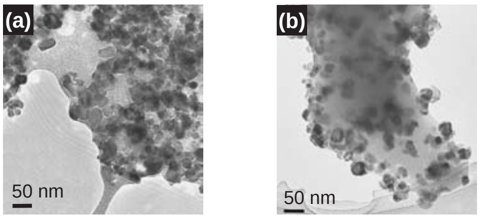


Figure 2. TEM images of (a) PDMS–titania hybrid and (b) PMMA–titania hybrid.

It is worth noting, additionally, that the surface complexation of urushiol moieties onto the titania surface was retained, since the UV–vis spectra of the hydrosilylated and graft-polymerized products (Figures 1c and 1d) show no shift in the position of the peak centered at 420 nm for the ligand-to-metal charge transfer.

In conclusion, we succeeded in immobilizing the C=C groups onto titania particles by surface complexation of urushiol. The C=C groups successfully underwent hydrosilylation and radical graft-polymerization to form PDMS–titania and PMMA–titania hybrids in which the titania particles were dispersed. These results indicate that surface complexation can be employed to prepare polymer–metal oxide hybrids.

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