

Surface Modification on Nanoscale Titanium Dioxide by Radiation: Preparation and Characterization

Bo Jiang,¹ Xiaotao Zu,² Fangyuan Tang,³ Zhihong Wu,¹ Jian Lu,¹ Qingrong Wei,¹
Xingdong Zhang¹

¹Engineering Research Center for Biomaterials, Sichuan University, Chengdu, Sichuan 610064, People's Republic of China

²Department of Applied Physics, University of Electronic Science and Technology of China, Sichuan 610054, People's Republic of China

³Key Laboratory for Radiation Physics and Technology of Education Ministry, Institute of Nuclear Science and Technology, Sichuan University, Chengdu, Sichuan 610064, People's Republic of China

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ABSTRACT: Electron beam mutual radiation to induce graft polymerization has been carried out respectively, between nanoscale anatase- or rutile-titanium dioxide particles surface and methyl methacrylate (MMA). The composition and properties of surface modified titanium dioxide were investigated by a number of surface sensitive techniques: X-ray photoelectron spectrum (XPS), FTIR, X-ray diffraction (XRD), and NMR. Results of the technological measurements show how surface chemistry is affected throughout the surface modification process, finally leading to a complete and homogeneous vinyl compound overlayer on top of the titanium dioxide samples. In comparison with stereochemical structures of the graft molecular chains and the PMMA induced by radiation polymerization, the surfaces of the oxides are considered to provide a template for the graft

polymerization. The grafted titanium dioxide is found to produce a stable colloidal dispersion, in good solvents for the grafted polymer, and the dispersibility of grafted dioxides is influenced by temperature. In addition, the wettability of the surface of titanium dioxide to water is readily controlled by grafting of hydrophilic or hydrophobic polymers. Based on the above results, it is concluded that MMA is covalently linked to the surface of titanium dioxide by a surface modification process. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3510–3518, 2006

Key words: nanoscale titanium dioxide; MMA; radiation induced; graft polymerization; surface modification; nano-composites

INTRODUCTION

Titanium dioxide has been intensively studied because it has excellent optical transmittance and high refractive index. It has been applied widely in optical and protective coatings, optical fibers, and photocatalysts.¹ Furthermore, nanoscale titanium dioxide, especially anatase nano-titanium dioxide, as a biomaterial, has many desirable properties, such as biological corrosion resistance, bacterial resistance, and self-cleaning, as well as physicochemical stability and security of organism. The nano-composites that blend the nanoscale oxide and a biomedical polymer, such as dental resin, can be made into functional inorganic-organic biomedical composites or other coating materials for oral and dental surgery. It was even shown that subcutaneous injection of an ultrafine titanium dioxide slurry with a stable dispersion, and subsequent near UV illumination, could slow and halt the

development of tumor cells.^{2,3} Fujishima and colleagues first discovered the photocatalytic splitting of water on titanium dioxide electrodes.⁴ They also found photocatalytic sterilization and photo-induced superhydrophilicity on titanium dioxide.⁵ By far the most actively pursued applied research on titanium dioxide is its use for photo-assisted degradation of organic molecules.^{6–10} Titanium dioxide is a semiconductor and the electron-hole pair that is created upon irradiation may separate and the resulting charge carriers might migrate to the surface where they react with adsorbed water and oxygen to produce free radical species. These attack any absorbed organic molecules and can, ultimately, lead to complete decomposition into carbon dioxide and water.¹ By utilizing the property of nanoscale titanium dioxide, new biomedical composites and coatings with bacterial resistance and self-cleanness can be prepared.

It becomes necessary to improve its surface properties for obtaining satisfactory and functional biomedical materials. A composite material is one in which two or more distinct, structurally complementary substances, combine to produce structural or functional

Correspondence to: B. Jiang (bojiangchem@email.com).

properties not present in any individual component. It is well known that the best properties of composite materials can be achieved when strong interaction exists between filler surface and polymer molecules. Surface modification is an important method in practical application of titanium dioxide because the oxide is often used as a component of biocomposites or coatings. Organic modifying agents are used to improve surface wettability and dispersibility of nano-titanium dioxide particles, while inorganic wrapping agents are used to improve the endurance and chemical stability of nano-titanium dioxide particles. However, many organic coupling agents with excellent properties cannot be used in biomedical materials because of their potential chronic cytotoxicity. The dispersibility of ultrafine inorganic particles in polymer or other organic matrices is known to be remarkably improved by the grafting of polymers onto these surfaces.¹¹ In fact, polymer chains grafted onto the surface are considered to interfere with the aggregation of particles and increase the affinity of the surface for the solvents and polymer matrices. Many studies on graft polymerization of vinyl monomers to inorganic compound materials employ treatment by surfactants with functional groups; the graft polymerization is then initiated through these groups on the surface of the inorganic materials.^{12–17} Obviously, the methods of indirect graft polymerizations are relatively fussy, and easily introduce low molecular weight compounds that possess potentially cytotoxic reaction. Ionizing radiation is a direct, effective, attractive method for contacting inorganic–organic materials interface and modifying surfaces of inorganic materials compared with other initiating means of graft polymerization.^{18,19} The grafting reaction also prepares biofunctional materials with cell recognizability. The grafted products not only possess a stable inorganic backbone, but also have some special functional groups, such as RGD and collagen, of grafting chains.^{20–25}

To investigate the role of surface modification on nanoscale titanium dioxide by the radiation graft method, to improve its surface properties, the research conclusions in this paper show that the methyl methacrylate (MMA) is covalently linked to the surface of titanium dioxide by a high energy electron beam induced process. Dispersibility and surface wettability of modified particles are discussed in the present work.

METHODS

Materials

Nanoscale titanium dioxide was purchased from Chinese Zhejiang Zhoushan Mingri Nano-materials Ltd. Company. Average diameter of globular anatase titanium dioxide was 20 nm, and the specific surface area

was greater than 200 m² g⁻¹. Average dimension of acicular rutile titanium oxide was 40 nm × 10 nm, and the specific surface area, greater than 150 m² g⁻¹. Both were dried over 12 h at 150°C, and then dried in vacuo for 8 h at 120°C.

Methyl methacrylate (MMA), which was purchased from Chinese Shanghai First Chemical Work of Reagent, was distilled at reduced pressure, and then preserved at low temperature.

All other reagents were analytical pure, and were used without further purification after removal of water.

Graft polymerization of vinyl monomers induced by EB irradiation

Appropriate solutions containing 20% of MMA, whose solvent was a mixture of *n*-heptane and chloroform with volume ratio 2–3, and treated titanium dioxide were placed in glass shallow containers. The mixtures in glass shallow containers were degassed in the degasser, and then filled with dry nitrogen at low temperature. Shallow containers of the nitrogen atmosphere conditions were sealed off with polyethylene film. The samples were irradiated by an electron beam from an electron accelerator of 1.7 MeV at controlled temperatures.

The absorptive dose equation of accelerator is expressed as follows:

$$D = \frac{F(R)EI}{LVS_p} \times 10^3$$

where D is absorptive dose in Gy. E is electron energy in MeV, I is electron beam current in μA , L and ρ are separately thickness (in cm) and density (in g cm⁻³) of coating membranes. V and S are separately rate (cm s⁻¹) and width (cm) of electron beam scanning. $F(R)$, which is characteristic absorptive coefficient, is obtained as follows:

$$R = \frac{\rho P N_0}{E} \sum f_i(Z/A)_i$$

Z , A , and N_0 are separately atomic number, atomic weight, and Avogadro constant. Looking up $F(R)$ – R curve will give the characteristic absorptive coefficient value after R value is calculated.

Determination of percentage of grafting yields

For obtaining graft materials and calculating exactly graft yield from the reaction mixture containing ungrafted polymer, two separate methods were utilized. The irradiated samples were extracted to constant weight by a mixture of dimethylbenzene and tetrahy-

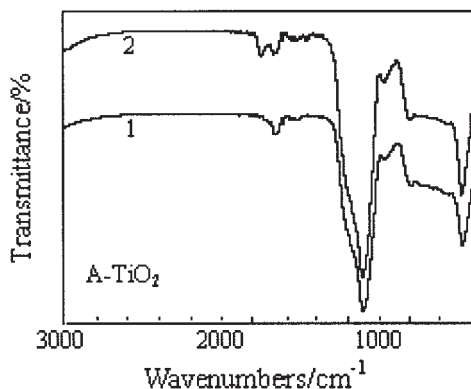


Figure 1 IR spectrum of anatase titanium dioxide. Curve 1: Anatase-TiO₂. Curve 2: TiO₂-g-MMA (graft yield: 15.8%).

drofuran (THF) in an extractor. Alternatively, the product was dispersed in a good solvent, such as THF, for grafted polymer and the dispersion was allowed to centrifuge at 1.0×10^4 rpm at 5°C. The titanium dioxide precipitated was dispersed again in good solvent for grafted polymer and centrifuged. The procedures were repeated until no more polymer could be detected in the supernatant solution. In comparison with grafting yields, approximate values were obtained by the two measurement methods.

Infrared spectrum measurement

IR Spectrum measurement was recorded by Nicolet 20SXB FTIR spectrophotometer. The solid samples were dispersed in KBr pellets.

X-ray photoelectron spectrum measurement

X-ray photoelectron spectrum measurement was recorded by a XSAM800/Series 800SIMS instrument.

X-ray diffraction measurement

XRD measurement was performed by Philips X'pert pro MPD meter. The operational conditions were working voltage, 50 kV, and electrical current, 30 mA, and Cu target Ka ray ($\lambda = 0.15406$ nm).

¹H-Nuclear magnetic resonance measurement

The graft polymethyl methacrylate (PMMA) was obtained by decomposing the graft material with hydrochloric acid of concentration 6 mol L⁻¹ to remove titanium dioxide for obtaining graft polymer, followed by precipitation in methanol. NMR measurement was performed by a Jeolfx-90Q meter. Deuterium chloroform was the solvent, and TMS was the reference criterion in experiments.

Dispersive stability of polymer-grafted titanium dioxide

Grafted titanium dioxides (0.50 g) were dispersed in 100 mL of good solvent for grafted polymer under stirring with a magnetic stirrer, and the dispersion was allowed to stand at different temperatures. After a definite time, 5.0 mL of dispersion liquid was taken out with a pipette, and the content of titanium dioxide dispersed was determined. The stability of dispersion was estimated from percentage of dispersed titanium dioxide after standing, by the following equation:

$$\text{Titanium dioxide dispersed (\%)} = (a/b) \times 100$$

where a (g) and b (g) are the weight of titanium dioxide dispersed after and before standing, respectively.

Wettability of surface of nanoscale titanium dioxide grafted MMA to water and polymers

The wettability of grafted titanium dioxide surface to water was estimated by the contact angle measurement of two-liquid methods.²⁶ After the grafted materials were pressured into thin slices, normal-hexane, normal-octane, normal-decane, and normal-hexadecane were used as reference liquids, and water was the soak liquid. According to the Young-Duprc formula and Fowkes theory, the contact angles of water were determined in the presence of normal alkanes. The grafted nanoscale titanium dioxide blends with PE, PVC, and PMMA for calculating the equilibrium adhesive work, the cohesion work, and the interfacial tension.²⁷

RESULTS

Figures 1 and 2 are infrared spectra of two nanotitanium dioxides before and after graft reactions induced by radiation. Spectral band 1 in Figure 1 is the infrared spectrum of anatase nano-titanium dioxide,

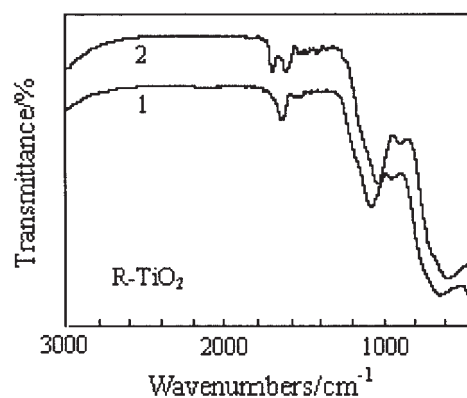


Figure 2 IR spectrum of rutile titanium dioxide. Curve 1: Rutile-TiO₂. Curve 2: TiO₂-g-MMA (graft yield: 11.9%).

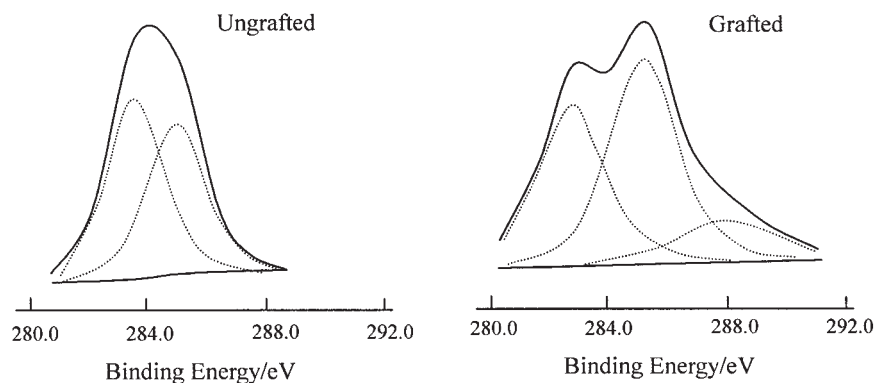


Figure 3 X-ray photoelectron spectrum of C_{1s} before and after graft polymerization. Ungrafted: anatase- TiO_2 . Grafted: anatase- TiO_2 -g-MMA (graft yield: 8.5%).

and band 2 is the infrared spectrum of product grafted MMA. In comparison with spectral band 1, new peaks at 1724 cm^{-1} , which are due to absorption of stretching vibration of carbonyl groups, appeared in the grafted product. However, corresponding absorptive peaks of PMMA by radiation polymerization are located at 1730 cm^{-1} . Absorptive peaks in 1630 cm^{-1} of anatase nano-titanium dioxide are simultaneously moved to 1645 cm^{-1} in spectrum 2. Analogously, Spectra 1 and 2 in Figure 2 are respectively, infrared spectra of rutile nano-titanium dioxide and rutile nano-titanium dioxide grafted MMA. Absorptive band of carbonyl group in graft materials moved from 1730 to 1725 cm^{-1} in spectrum 2, and absorptive peaks 1631 cm^{-1} in rutile nano-titanium dioxide are simultaneously moved to 1645 cm^{-1} in spectrum 2. Therefore, comparing spectrum 1 in Figures 1 and 2, the shape and the related intensity of the titanium dioxide and the MMA have all changed in spectrum 2. The grafted products all show some new characteristic peaks in the infrared spectrum. The experimental results of IR spectra indicate the presence of chemical bonding between titanium dioxide and grafted organic compound MMA.

X-ray photoelectron spectrum (XPS) analysis is used to measure the surface composition of ungrafted and grafted samples. To testify further the existence of chemical bonding at the interface of nano-titanium dioxide and MMA, XPS spectra of anatase nano-titanium dioxide before and after graft polymerization were measured. Figure 3 is XPS narrowband scanning chart of C_{1s} . The solid line in the figure is the experimental curve, and the point line is a Gauss simulant curve. Carbon element in nano-titanium dioxide before graft polymerization is introduced in testing process for comparison with product after graft polymerization, and the 284.9 eV of carbon-carbon bond is used as a reference criterion. Compared with XPS of ungrafted sample, the spectrum of grafted sample is obviously broad, and produced a new spectrum at

288.1 eV of dibond of carbon-oxygen. The C_{1s} peak similar to the reference criterion also appeared at 283.7 eV because of graft onto nano-titanium dioxide.

XRD spectra of nano-titanium dioxide particles show that the two ultrafine powers are respectively, single anatase and rutile nano-titanium oxide particles from Figure 4. Employing linear analytical methods of XRD, the average granular diameters of the samples are calculated with the Debye-Scherrer formula according to half width high of the diffraction peak in titanium dioxide samples after deducting from width of instruments. The average granular diameter of anatase titanium oxide was 12 nm , and that of rutile nano-titanium oxide was 17 nm . The results are close to values of specific surface areas, that anatase titanium oxide particles are $200\text{ m}^2\text{ g}^{-1}$, and rutile nano-titanium oxide particles are $150\text{ m}^2\text{ g}^{-1}$, data provided by the producer. Determining the percentage of grafting yields in different radiation dosages, the grafting yields increase with the increasing radiation dosages, and the grafting yields of anatase nano-titanium oxide are greater than those for rutile structured oxide in our experimental conditions in Figure 5. This shows that it

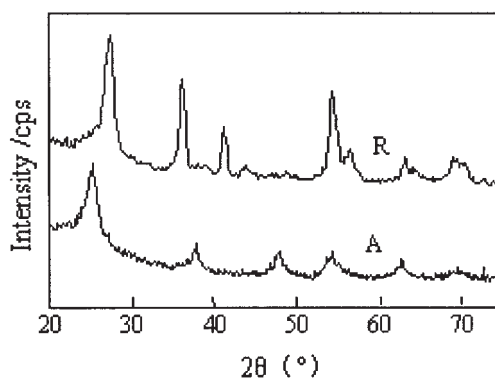


Figure 4 XRD of nanoscale titanium dioxide: Anatase- TiO_2 ; Rutile- TiO_2 .

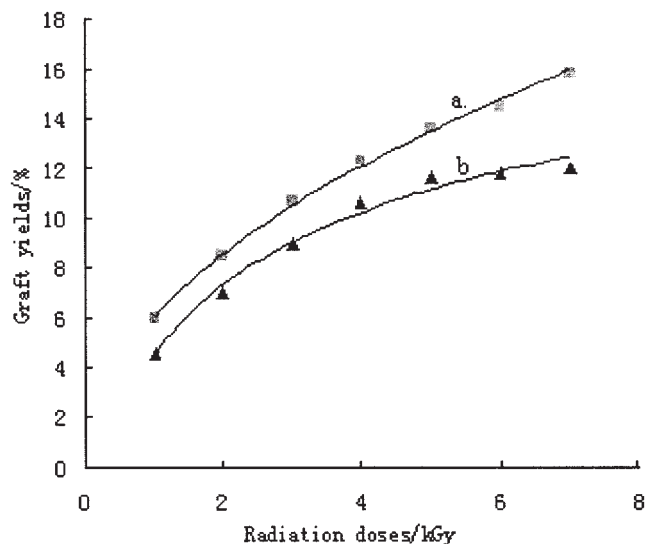


Figure 5 Graft yields obtained by extracted method of different compounds: (a) Anatase-TiO₂ and (b) Rutile-TiO₂. Atmosphere condition: nitrogen; Temperature: 5°C.

is a typical graft polymerization controlled by kinetic processes.

Surface structure of nano-titanium dioxide plays an important role in graft polymerization. All organic monomers are first absorbed onto inorganic materials because of the tremendous surface areas of nanoscale particles. Employing deuterated chloroform as solvent, and TMS as reference criterion in the experiment, NMRs of PMMA were measured. Spectral a and b in Figure 6 are, respectively, ¹H-NMR spectrum of the grafted PMMA, obtained by decomposing the graft materials and the PMMA from radiation poly-

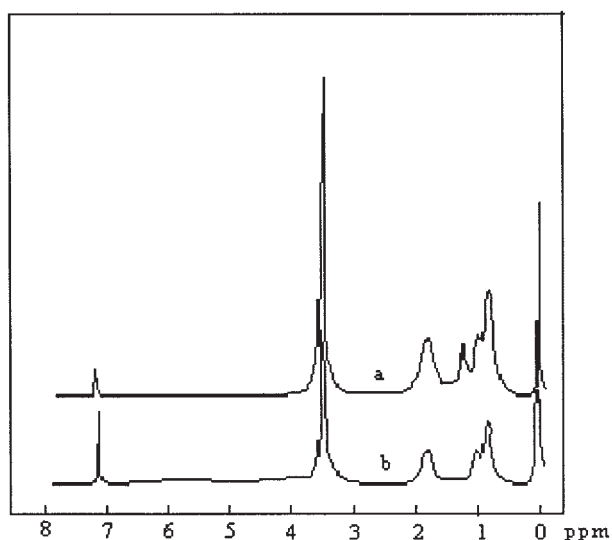


Figure 6 ¹H-NMR spectra of PMMA. (a) PMMA comes from radiation polymerization. (b) PMMA comes from graft links.

TABLE I
Percentage of Dispersible Stability in THF^a

Time (hr)	Ungrafted (at 25°C; %)	Grafted (at 0°C; %)	Grafted (at 25°C; %)	Grafted (at 50°C; %)
0	97.1	98.2	100	100
24	2.8	70.2	78.5	88.4
48	2	64.8	67.3	71.3
72	1.7	60.5	59.4	50.6
96	1.1	57.3	57.5	50.1

^a Anatase titanium dioxide and grafted titanium dioxide of graft yield for 15.8%.

merization. The figure shows that the PMMA coming from radiation polymerization is obviously different from PMMA of the irradiated samples. Spectrum a in Figure 6 is the NMR of PMMA from radiation polymerization. There are obviously three different hydrogen atoms, which are α -methyl, methylene and methoxyl, in the PMMA molecule. 7.287 ppm is, here, solvent peak, and 3.599 and 1.837 ppm are separately resonant peaks of methoxyl and methylene. 1.262 and 1.032 and 0.853 ppm are all resonant peaks of α -methyl. Peaks of 1.262, 0.853, and 1.032 ppm are recognized to be respectively, isotactic, syndiotactic, and atactic sequences. According to the relative strengths of absorptive peaks in the spectrum, the proportion of the several peaks of PMMA by radiation polymerization is that the isotactic sequence is most, and the syndiotactic and atactic sequences are approximately equal. Comparing NMR of PMMA from radiation polymerization with of PMMA grafted on titanium dioxide surface, spectrum b in Figure 6, all peaks are not displaced, but the isotactic sequence disappears and the proportion of the syndiotactic sequence and the atactic sequence increases. The surface arrangement order of inorganic compounds is a template to absorbed monomers.

The stability of dispersion is estimated from percentage of dispersed titanium dioxide after standing, shown in Table I. As compared with ungrafted titanium dioxide, dispersible stabilities of the oxide modified by graft polymerization give a stable colloidal dispersion in THF. The grafted polymer chains on the surface interfere with aggregation of the titanium dioxides, in good solvents for the grafted polymer, so that the surface wettability is increased, and the dispersibility of grafted dioxides is influenced by temperature, as shown in the table.

The wettability of polymer-grafted titanium dioxide surface to water in the presence of normal alkanes is estimated by contact angle measurement. According to Young-Dupre formula and Fowkes theory, the contact angles of water, in which normal alkanes (such as normal-hexane, normal-octane, normal-decane, and normal-hexadecane) are used as referenced liquids, are measured. Figure 7. is the relationship of graft

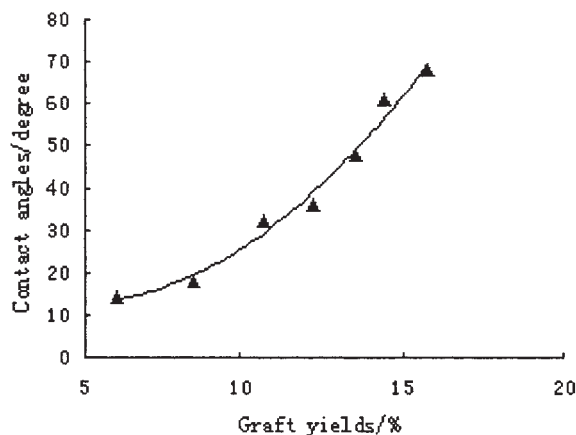


Figure 7 Relationship of graft yields and contact.

yields and contact angles of water in normal hexane as reference liquids. The angles of water are different from one another at the same graft yield with different reference liquids. But with graft yields increasing, the contact angles increase. So, surface modification on nano-titanium dioxide by radiation graft is obvious. The surface free energies of polymer-grafted titanium dioxide are calculated as follows:

$$\gamma_W - \gamma_H + \gamma_{HW} \cos \theta_{SW/H} = 2(\gamma_S^d)^{1/2} [(\gamma_W^d)^{1/2} - (\gamma_H^d)^{1/2}] + I_{SW}^p \quad (1)$$

$$\gamma_S^p = (2I_{SW}^p)^2 / \gamma_W^p \quad (2)$$

where $\theta_{SW/H}$ is contact angle of water to solid in the presence of alkanes. γ_W and γ_W^d are separately surface free energy of water and dispersion component. γ_H and γ_H^d are separately surface free energy of alkanes and dispersion components. I_{SW}^p is the polar component of surface free energy. γ_S^p is the polar component of surface free energy of solid. The contact angles of water to solid, in the presence of alkanes, are first measured, and then, a beeline is drawn with $\gamma_W - \gamma_H + \gamma_{HW} \cos \theta_{SW/H}$ versus $(\gamma_W^d)^{1/2} - (\gamma_H^d)^{1/2}$. Dispersion components and polar components of solid surface free energy are calculated with slope and intercept from the line. Table II shows calculated values of

TABLE II
Surface Energies and Components of Anatase Titanium Dioxide and Grafted Produces at 25°C

Graft yields (%)	γ_S^p (mJ m ⁻²)	γ_S^d (mJ m ⁻²)	γ_S (mJ m ⁻²)
0.00	48.23	26.45	74.68
8.50	46.82	23.16	69.98
10.70	37.32	20.89	58.21
13.60	33.86	18.32	52.18
15.80	28.12	11.46	39.58

TABLE III
Equilibrium Adhesive Work and Cohesion Work and the Interfacial Tension of Modified Anatase Titanium Dioxide of Graft Yield at 29.18%

	W_A (mJ m ⁻²)	W_C (mJ m ⁻²)	γ_{SL} (mJ m ⁻²)
PE	72.41	84.01	45.77
PVC	78.11	128.28	50.24
PMMA	99.43	144.37	36.95

the surface free energy γ_s and the polar component γ_s^p and the dispersion component γ_s^d in different graft yields.

Three polymers of PE, PVC, and PMMA were selected as mold materials, since resins used by oral and dentistry surgery mainly contain vinyl compounds. If we use the nano-titanium dioxide modified by MMA blends with PE, PVC, and PMMA in nano-composites, according to surface free energies data of PE, PVC, and PMMA provided by literature,²⁶ the formulae of the equilibrium adhesive work W_A , and the cohesion work W_C , and the interfacial tension γ_{SL} are calculated as follows:

$$W_A = 2[(\gamma_s^d \gamma_L^d)^{1/2} + (\gamma_s^p \gamma_L^p)^{1/2}] \quad (3)$$

$$W_c = 2\gamma_{LV} \quad (4)$$

$$\gamma_{SL} = [(\gamma_s^d)^{1/2} - (\gamma_L^d)^{1/2}]^2 + [(\gamma_s^p)^{1/2} - (\gamma_L^p)^{1/2}]^2 \quad (5)$$

The equilibrium adhesive work, the cohesion work, and the interfacial tension are shown in Table III after the modified titanium dioxide blends with PE, PVC, and PMMA.

DISCUSSION

Surface modifications, which can improve the interface compatibility between inorganic and organic materials, are often required for material surfaces with some special elements or various active groups. Although many studies on graft polymerization of vinyl monomers to inorganic materials by various initiating methods have been published, it is generally quite difficult to initiate graft polymerization on the surface of inorganic materials with common chemical initiating methods. Ionizing radiation can directly activate a substance, and induce graft polymerization of vinyl monomers in some particular conditions.^{18,19}

Determinations of grafting yields will primarily estimate feasibility of the surface modification method. Two processes, in which extraction at high temperature, and in which dispersing and centrifugation in a good solvent of graft organic chain at low temperature, are utilized, in order that dependability of testing data is ensured. In fact, the obtained experimental

data themselves under different conditions have proved to be not simply adsorption and coating on the inorganic material surfaces. Infrared spectra of anatase and rutile nano-titanium dioxides after graft reactions have further shown that absorptive peaks of stretching vibration of carbonyl group of grafted organic polymeric chains appear at 1724 or 1725 cm^{-1} : the corresponding peaks of PMMA with radiation polymerization are at 1730 cm^{-1} in Figures 1 and 2. Absorptive peak sites after graft polymerization are moved to lower wavenumbers. This is because the strongest titanium–oxygen chemical bond (—O—Ti—O—) of titanium dioxide makes density of the electronic cloud in grafted organic molecules decrease, and also decreases the force constant among atoms. Similarly, there are absorptive peaks of 1645 cm^{-1} sites in ungrafted titanium dioxide; corresponding peaks are moved into 1630 and 1631 cm^{-1} after graft polymerization. In comparison with ungrafted oxide, relative strengths and sites and shapes in infrared spectra of the grafted produces have changed. It is an obvious conclusion that each are influenced by the presence of chemical bonds between inorganic and organic substances and different from a common mixture of the two materials. For further research on the relationship between titanium dioxide and grafted organic chains, with XPSs of nano-titanium dioxides before and after graft reactions show the binding energy of $\text{C}_{1\text{S}}$ as shown in Figure 3. The binding energy of $\text{C}_{1\text{S}}$ deviates at 285 eV site in the grafted substance, and the energies become gradually smaller as the graft yields increased. The binding energies of $\text{O}_{1\text{S}}$ moved to higher energy as the graft yields increased. This is further evidence of the presence of covalent bond between the oxygen atom in titanium dioxide crystal the and β -carbon atom in MMA. The density of electric charge between oxygen atom in titanium dioxide crystal and β -carbon atom in MMA moves to the β -carbon because the electron density of β -carbon atom is effected by carboxyl groups of MMA. Therefore, the value of binding energy of $\text{C}_{1\text{S}}$ decreases, and $\text{O}_{1\text{S}}$ increases.

In previous papers, we have reported mechanism of graft reaction of vinyl polymers onto magnesium oxide and activated alumina initiated by surface radicals formed by radiation.^{18,19} Further, according to our experimental observation, the graft polymerization is a kinetic controlling process too. Compared with graft yields of congener materials of different specific surface areas in the same radiation conditions, the graft yields are obviously affected by the specific surface area and the absorbent capacity of oxide surface and the diffusive rate of vinyl monomer in the isophase graft polymerization in Figure 5. A larger specific surface area of materials favors graft polymerization of vinyl monomers on inorganic materials, which not only increases the absorbing quantity to monomers

but also benefit monomer diffusing into surface of inorganic substances. So, the bigger the specific surface areas are (for example, the anatase nano-titanium oxide particles are 200 $\text{m}^2 \text{g}^{-1}$, and the rutile nano-titanium oxide particles are 150 $\text{m}^2 \text{g}^{-1}$) the bigger the differences of chemical bonds and electronic states on surfaces are with inner nanoscale particles. Because ligands on surface atoms are incongruent in comparison with inner atoms of the particles, the surface activated centers increase after irradiation. Therefore, the graft yields of the oxide surface are augmented. The experimental facts embody fully the surface effect of nano-materials. NMR spectra of PMMA coming from the radiation polymerization and the grafted produce confirm the template effect of material surface. The spectra not only show organic monomer grafted on the oxide surface, but also demonstrate that the first of the graft polymerization is monomers absorbed on surface of solid. The three-dimensional structures of graft chains are controlled by surface properties of the oxide.

Although some mechanisms of graft polymerizations induced by ionizing irradiation have been discussed, most mechanisms are still obscure, and many inorganic compound materials cannot be induced to graft polymerization with this method under our experimental conditions. Because the grafted inorganic materials are made from different elements and compositions, and have different radiation chemical effects, the graft reaction mechanisms could be different from one another.^{18,19,28,29} With regard to compounds with empty orbit atoms, such as aluminum and titanium atoms, it is believed that they lose an oxygen atom by which compounds with aluminum atoms produce a radiation defect in aluminum oxide (Al_2O_3) by irradiation. One electron of the double bond is opened in vinyl monomers, is coordinated to the aluminum atom and the other initiates free radical graft polymerization of MMA on the surface. Grafting polystyrene onto sorbate-modified titanium dioxide surface provide similar grafting between titanium atom and sorbate.¹⁴ The mechanisms in the reaction system might be as illustrated in Figure 8. Of course, as discussed above, the electron-hole pair that is created upon irradiation with electron beam may separate and the resulting charge carriers might migrate to the surface to produce free radicals species where they react with adsorbed vinyl monomers and initiate graft polymerization. In other words, surface graft polymerizations induced by radiation are relative to the properties of the surface area of materials and the crystalline property and the radiation effect of inorganic solid.

Wettability and dispersive stability are always of primary concern when designing biomedical devices using a new method of surface modification. Because nano-titanium dioxide, modified by the radiation graft

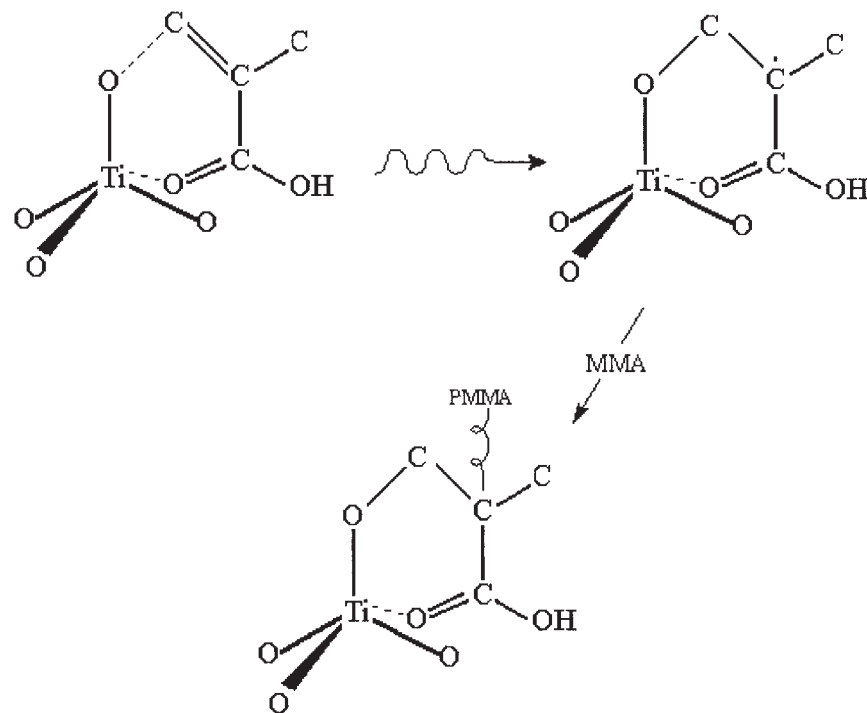


Figure 8 Schematic diagram of the reactions occurring in the reaction system when subjected to electron beam irradiation. The scheme only highlights the most favorable reactions.

method, is used in biomedical gels or coatings or composites, its stability and wettability to organic materials are very important aspects to be evaluated. The experimental data prove that dispersive stability of the graft product reached 78.5% in a good solvent, such as THF, of PMMA after 24 h at 25°C. Wettability of polymer-grafted titanium dioxide surface to water proves the successful modification of the surface of ultrafine particles. This fact also shows that the modification method enhances the affinity of the oxide surface. Surface free energy is intermolecular, including tropic and derivational and dispersive forces. The intermolecular forces are stronger because of the presence of strong polar groups in the graft product. It is obvious that surface free energies are decreased because polar components are decreased and dispersion components are increased. Polymeric polarities from PE and PVC to PMMA increase in turn, and the equilibrium adhesive work and the cohesion work also increase, as shown in Table III. The interfacial tension of PMMA is the lowest, i.e., surface free energies and components of PMMA blended with of grafted nanotitanium dioxide match better. Conclusions of theoretical calculations show the presence of the best compatibility between PMMA and grafted produce, and accord with experimental fact too. Considering the untreated sample, the detected value is in good agreement with literature on titanium dioxide surfaces in general and, in particular, on blends with dental resins. Briefly, MMA is covalently linked to the surface of

titanium dioxide by a surface modification process, so that the surface of titanium dioxide is covered by a thin organic layer.

CONCLUSIONS

Based on the above results, it is concluded that MMA is covalently linked to the surface of nanoscale titanium dioxide by the surface modification method of radiation grafting. The isophase graft polymerization is a kinetic controlling process. The specific surface area and the absorbent capacity of oxide surface and the diffusive rate of vinyl monomer influence the reactive graft yields. The surface structures of the oxides have especially an influence on stereochemistry of graft polymeric chain; the structure responds to the environment. These results confirm the hypothesis that the radiation graft polymerization on nanoscale titanium dioxide surface is a sensitive method. The data discussed about wettability and dispersive stability in this paper support feasibility and dependability of grafted produce and processes. The grafting reaction is also used in preparing biofunctional materials with cell recognizability. In practice, immobilized biomolecules, such as RGD or collagen, and the overall interfacial structure increase the information contact of the surface and the degrees of freedom as compared with those of the inorganic surface. Titanium dioxide modified by radiation graft according to the present process is safe, both at an *in vitro* and an *in vivo* level.

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