

# Preparation and Characterization of Acrylic Resin/Titania Hybrid Nanocomposite Coatings by Photopolymerization and Sol–Gel Process

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**ABSTRACT:** Titania-containing coatings were prepared through a dual-cure process involving radical photopolymerization of a polysiloxane diacrylate and subsequent condensation of alkyltitanate groups. The kinetics of photopolymerization and condensation reaction was investigated as a function of the inorganic phase precursor (titanium tetraisopropoxide) content. AFM analysis gave evidence of a strong interaction between the organic and inorganic

phase with the formation of titania domains in the nanoscale region. An increase of hydrophilicity in the coatings surface with increasing TiO<sub>2</sub> content was evidenced. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4659–4664, 2006

**Key words:** hybrid nanocomposites; radical photopolymerization; coatings; AFM

## INTRODUCTION

Hybrid organic–inorganic nanocomposites have drawn considerable attention, in recent years, because they combine both the advantages of organic polymer (flexibility, lightweight, good impact resistance, and good processability) and inorganic materials (high mechanical strength, good chemical resistance, thermal stability, and optical properties).<sup>1</sup>

An interesting method for obtaining these hybrid materials is the *in situ* sol–gel process, which allows to obtain metal-oxide domains in a polymer network;<sup>2</sup> it involves a series of hydrolysis and condensation reactions starting from hydrolysable multifunctional metal-alkoxides as precursors for the inorganic domain formation.<sup>3</sup> A coupling agent to the organic matrix is usually added to provide bonding between the organic and inorganic phases preventing macroscopic phase separation. Under the proper conditions, the size of the inorganic particles can be reduced to nanometric dimension.<sup>4</sup>

Although the majority of the papers report about the *in situ* formation of silica in a polymeric matrix,<sup>3,5–10</sup> organic–inorganic hybrids based on titanium dioxide prepared by the sol–gel process is attracting increasing attention only in the recent years.<sup>1,11–14</sup>

Titanium dioxide nanoparticles containing polymers (nanohybrids) are characterized by unique mechanical, thermal, surface, optical, and electronic properties.<sup>15,16</sup> In addition, TiO<sub>2</sub> imparts to the polymer matrix a high refractive index<sup>11</sup> and is also characterized in specific crystalline states (Anatase) by photocatalytic properties, which are effective for the inactivation of microorganisms.<sup>17</sup>

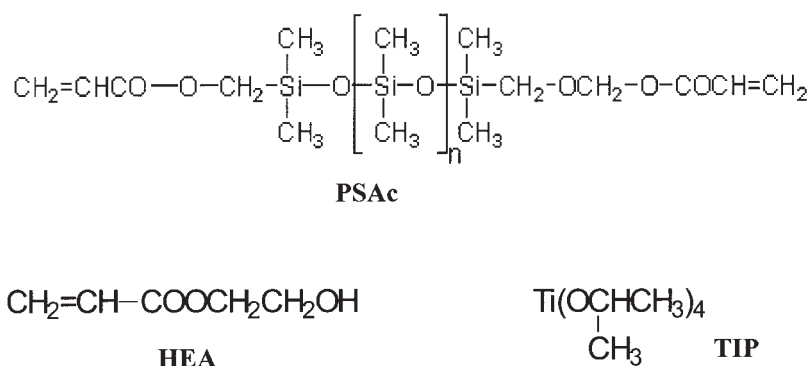
In this context, we considered the preparation of titania-containing hybrid materials by combining the sol–gel reaction with a photopolymerization process; this allows combining the advantages connected to both the curing methods.

The photopolymerization technique is getting more and more importance in the field of coatings;<sup>18</sup> it induces the polymer formation with a fast transformation of the liquid monomer into the solid film with tailored physical, chemical and mechanical properties, and it can be considered as an environment friendly technique due to the solvent free process usually carried out at room temperature.<sup>19</sup>

To our knowledge, there is only one paper in the literature reporting the use of titanium tetraisopropoxide (TIP) as TiO<sub>2</sub> precursor in a UV-curing technique.<sup>20</sup> We went further investigating the effect of TIP concentration on kinetics and properties of epoxy cationically UV-cured networks<sup>21</sup> compared with systems containing dispersed TiO<sub>2</sub> nanoparticles. We concluded that by TiO<sub>2</sub> *in situ* generation, in the presence of a suitable coupling agent and by subsequent UV photocuring (dual cure), it is possible to induce a homogeneous dispersion of the inorganic particles

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**Scheme 1** Chemical structure of the monomer employed. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

within the organic epoxy matrix avoiding macroscopic phase separation.

In this study, the  $\text{TiO}_2$  nanoparticles were prepared *in situ* by a sol-gel process within a radically UV-curable organic polymer. A polysiloxane diacrylate (PSAc) resin and a titania sol-gel precursor, TIP, were cured via a radical process. Hydroxyethyl acrylate (HEA) was used as a coupling agent to increase the interfacial interactions between the organic and the inorganic moieties, most likely via covalent bonds. The mixture was first subjected to UV curing and then to a thermal condensation of the alkoxy titanate groups. The properties of the cured system were evaluated and correlated to the titania content.

## EXPERIMENTAL

### Materials

Polysiloxane diacrylate (PSAc, Coatosil 3509,  $M_n = 2776$ ) was given from Osi Crompton Switzerland and it was used as acrylic photocurable resin. 2-Hydroxyethylacrylate (HEA), dibutyl tin diacetate and titanium tetraisopropoxide (TIP) were purchased from Aldrich and used as received; their chemical structures are reported in Scheme 1. The radical photoinitiator Darocure 1173 (2-hydroxy-2-methyl-1-phenyl propan-1-one, PI), was supplied from Ciba.

### Preparation of the hybrid samples

Different acrylate photocurable formulations were investigated with titania precursor content ranging from 0 to 50 wt %; the composition of the investigated

formulations are reported in Table I. In the different mixtures, 2 wt % of radical photoinitiator Darocur 1173 was added. In the case of hybrid mixtures containing the TIP precursor, 2 wt % of HCl and dibutyltin diacetate as condensation catalyst were added.

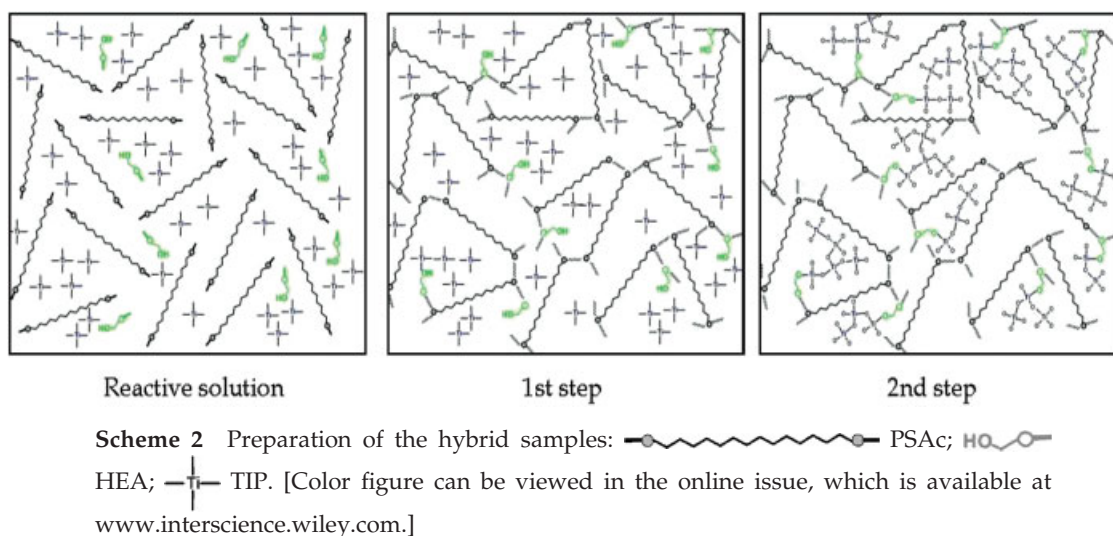
The liquid mixtures (reactive solution of Scheme 2), after 1 min of vigorous magnetic stirring at  $25^\circ\text{C}$ , were coated on different substrates (i.e., glass, PET) and photocured with a medium pressure mercury lamp (first step of Scheme 2), under nitrogen atmosphere for 2 min at a light intensity of  $30 \text{ mW}/\text{cm}^2$  on the sample surface. The subsequent hydrolysis and condensation reactions were performed storing the photocured films in an oven, at  $100^\circ\text{C}$  for 4 h, in a constant humidity controlled chamber (95–98% relative humidity obtained via a saturated solution of aqueous  $\text{NH}_4\text{H}_2\text{PO}_4$ , second step of Scheme 2). The obtained samples after thermal treatment appeared transparent and it was possible to prepare free standing films of about  $100 \mu\text{m}$ .

### Characterization technique

The kinetics of the photopolymerization was determined by real-time FTIR spectroscopy, employing a Thermo-Nicolet 5700 instrument. The liquid formulations were coated onto a silicon wafer by a wirewound applicator obtaining a  $25 \mu\text{m}$  thick film. The sample was exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam, which analyzes *in situ* the extent of the reaction. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Acrylic double bond

**TABLE I**  
Percentage Composition of Investigated Formulations

	PSAc-0	PSAc-10	PSAc-30	PSAc-50
Acrylic d.b. conv. (%)	100	90	62	26
Gel cont. after UV (%)	92	86	67	53
Gel cont. after therm. curing (%)	–	88	80	83
$T_g$ ( $^\circ\text{C}$ ) DSC	–38	–44	–52	–60



conversion was followed by monitoring the decrease in the absorbance due to acrylic C=C peak centered at  $1635\text{ cm}^{-1}$ . A medium pressure mercury lamp equipped with an optical guide was used to induce the photopolymerization (light intensity on the surface of the sample of about  $10\text{ mW/cm}^2$ ). Variation in the experimental conditions (light intensity, humidity, and temperature) caused slight differences in the kinetic curves. For this reason, all the conversion curves reported in one figure were performed on the same day and under the same conditions, thus good reproducibility was obtained.

The gel content was determined on the cured films by measuring the weight loss after 24 h extraction with chloroform at room temperature.

DSC measurements were performed with a DSCQ 1000 of TA Instruments equipped with a low temperature probe, under nitrogen flux, in the range between  $-80$  and  $150^\circ\text{C}$ .

TGA were performed using a LECO TGA-601 Instrument in the range between  $30$  and  $700^\circ\text{C}$ , with a heating temperature of  $10^\circ\text{C/min}$  in air.

The AFM measurements were done on the films coated on glass substrates in the tapping mode using a Dimension 3100 Nanoscope IV (Veeco, USA). A pointprobe silicon-SPM-sensor (Nanosensor, Germany) with spring constant of  $\sim 3\text{ N/m}$  and resonance frequency of  $\sim 75\text{ KHz}$  was used. The scan conditions were chosen according to Maganov et al.<sup>22</sup> (free amplitude  $> 100\text{ nm}$ , set-point amplitude ratio 0.5) to get stiffness contrast in the phase image that means bright features in the phase image are stiffer than dark.

Contact angle measurements were performed with a Krüss DSA10 Instrument, equipped with a video camera. Analyses were made at room temperature by means of the sessile-drop technique. Three to five measurements were performed on every sample and the values were averaged. The measuring liquid was doubled distilled water ( $\gamma = 72.1\text{ mN/m}$ ).

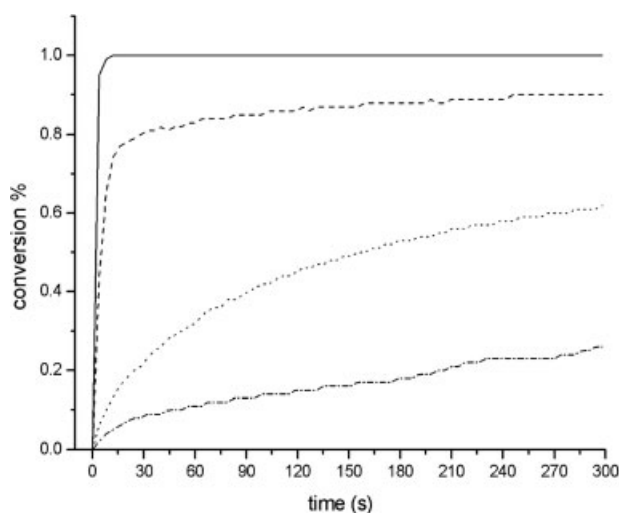
## RESULTS AND DISCUSSION

### Kinetic measurements

The effect of the presence of titanium TIP on the rate of photopolymerization of a polysiloxane diacrylate/hydroxylacrylate (4 : 1 ratio) mixture was investigated by means of FTIR in real time. The conversion curve as a function of irradiation time for the neat PSac-0 mixture is reported in Figure 1 and it is compared with the curves for the formulations containing increasing amount of TIP.

It is possible to observe that both the final conversion and the polymerization rate are affected by the presence of the tetraisopropyl-titanate with a significant decrease on acrylic double bond conversion and polymerization rate by increasing the TIP content.

The strong decrease on UV-curing conversion is attributable to the premature formation of  $\text{TiO}_2$  particles, during mixing. In fact, titanium TIP is very reactive



**Figure 1** Real time FTIR kinetic curves for psac-0 (—), and for hybrid systems containing 10% TIP (---), 30% TIP (···), and 50% TIP (-·-).

and the atmospheric humidity can induce fast hydrolysis and condensation reaction with  $\text{TiO}_2$  formation. Titania particles, even formed in minimal amounts, can absorb UV light in competition with the photoinitiator inducing a shielding effect, which prevents the complete cure of PSAc.

After photopolymerization, the thermal condensation reaction was followed by measuring the weight loss due to propanol evaporation. The maximum of the condensation curves was achieved after 4 h treatment in an oven at  $100^\circ\text{C}$  under constant humidity (95–98% relative humidity). In all the investigated systems, the experimental weight loss was lower but very close to the theoretical values. As stated earlier, this difference between the experimental and theoretical values could be due to a small degree of hydrolysis already taken place during mixing and photopolymerization.

The lower double bond conversion in the presence of TIP is reflected by a lower gel content of the UV-cured films (Table II). After thermal hydrolysis and condensation reaction, the gel content of the cured films increased significantly, due to the strength introduced by the inorganic domains formation and the assumed incorporation of some of the HEA-OH functions into the inorganic phase, but the effect of the lower acrylate conversion could not be fully compensated.

### Thermal properties

Thermal analysis performed on dual-cured films by DSC evidenced a decrease on  $T_g$  values by increasing TIP content in the photocurable formulation even after the condensation reaction (Table II). This behavior is in accordance with the FTIR data and attributable to the lowering of acrylic double bond conversion by increasing the TIP concentration.

Thermal stability of polymer networks was determined using a thermogravimetric analyzer. The TGA curves of pure polyacrylate and in the presence of an increasing amount of TIP are shown in Figure 2. Although there is almost no difference in their thermal stability, an increase on char content with increasing TIP concentration is evident for the hybrid systems in comparison to the  $\text{TiO}_2$  free formulation. The char content values are slightly higher than the expected theoretical values calculated from the initial composition, according to the sol-gel reaction. This is probably due to some silica char formation obtained from polysiloxane decomposition.

TABLE II  
Properties of Cured Films

Component	PSAc-0	PSAc-10	PSAc-30	PSAc-50
PSAc	80	72	56	40
HEA	20	18	14	10
TIP	0	10	30	50

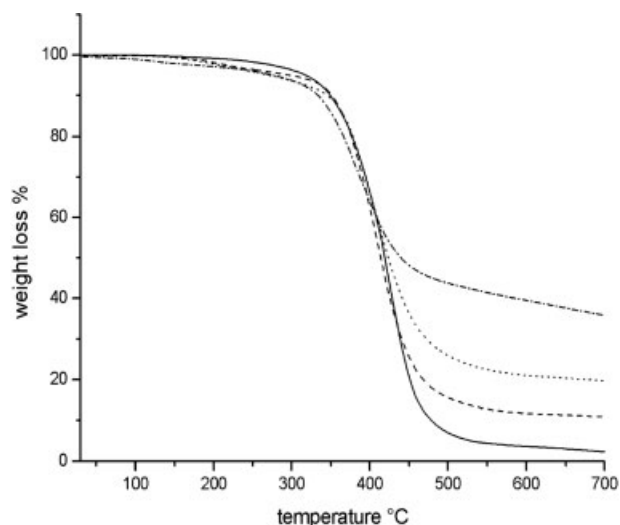


Figure 2 TGA thermograms for cured films PSAc-0 (—), and for hybrid systems containing 10% TIP (---), 30% TIP (···), and 50% TIP (-·-·).

### Morphology

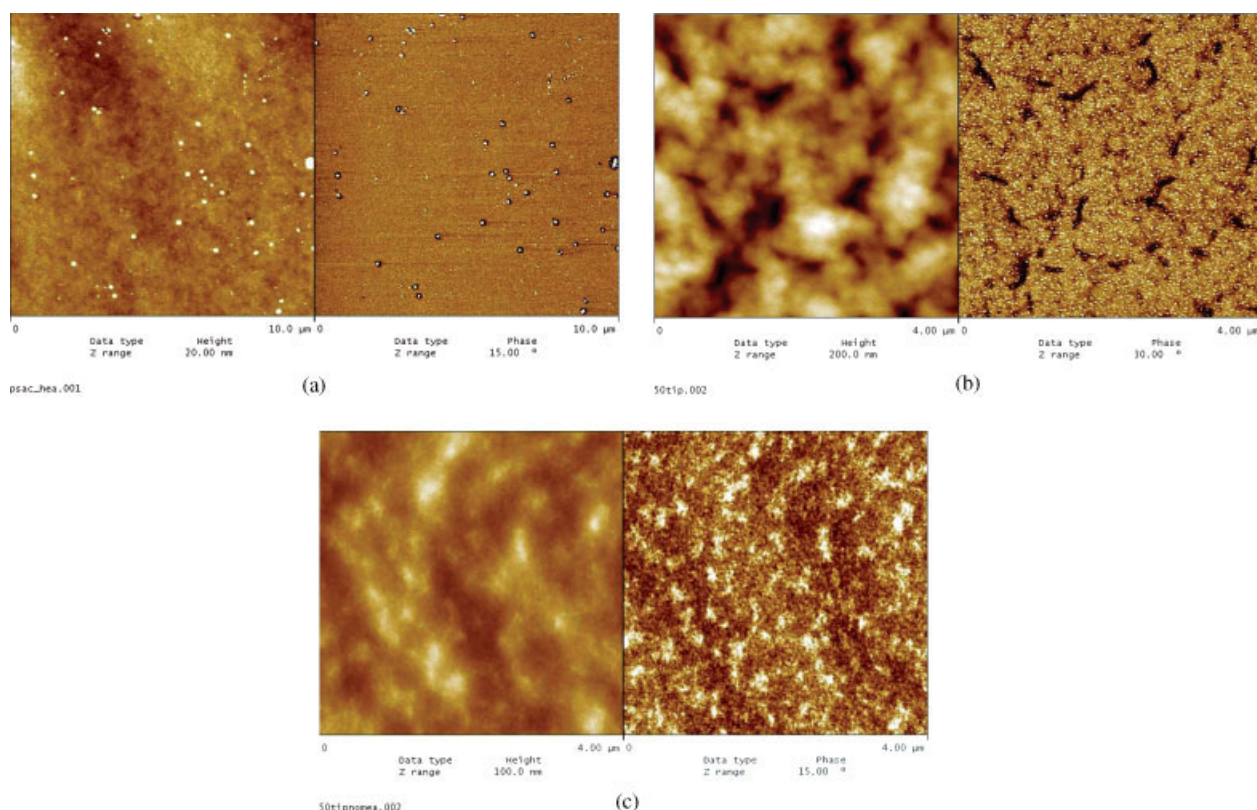
The dual-cured hybrid films were optically transparent, as shown in Figure 3. The transparency can be an evidence that the organic-inorganic phase separation is in the scale of smaller than 400 nm. The formation of inorganic domains in the nanometer range size was further confirmed by AFM analysis in topology and phase contrast images.

In Figure 4(a), the AFM images are reported for the  $\text{TiO}_2$  free photocured film. Figure 4(b) shows the images for the film obtained in the presence of 50 wt % TIP and Figure 4(c), the AFM images for the same formulation (containing 50 wt % TIP) cured without HEMA coupling agent.

It is possible to observe that the  $\text{TiO}_2$  free film is smooth while the presence of titania precursor in the



Figure 3 photograph of a hybrid film containing 50 wt % TIP.



**Figure 4** AFM image topology and phase contrast: (a) TiO<sub>2</sub> free cured film (containing some air bubbles); (b) hybrid film containing 50 wt % TIP and HEA; (c) hybrid film containing 50 wt % TIP without HEA. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

photocurable resin increases the surface roughness. In the phase contrast image of Figures 4(b) and 4(c), the small bright (hard) domains were attributed to the titania phase, while the dark (soft) domains belong to the polymeric network characterized by a low  $T_g$  ( $-60^\circ\text{C}$ ). Figure 4(b) shows that the organic and inorganic phases are fully interconnected with no major macroscopic phase separation, which might have occurred during the dual-curing process; the titania domains generated by sol-gel process are fully embedded into the polymeric matrix showing a nanometric domain size in the range of 15–25 nm.

The important role of HEMA as coupling agent is evident in Figure 4(c). In the absence of HEMA, the TiO<sub>2</sub> tends to form agglomerates giving rise to the formation of larger size inorganic domains. This is an evidence that HEMA, acting as coupling agent, can condense with its hydroxyl groups with titanate groups generated from TIP hydrolysis, and it can copolymerize with its acrylic double bond with the polymeric network. HEMA was previously successfully employed as coupling agent in the preparation of a series of sol-gel derived organic-inorganic hybrid materials consisting of organic polymethylmethacrylate and inorganic titania cured by classical thermal process.<sup>12</sup>

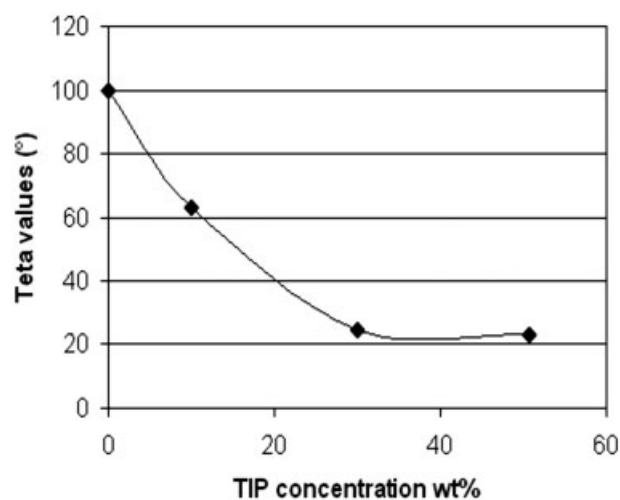
The strong chemical-bond interaction between the organic and inorganic domains, through HEMA coupling agent, are crucial to avoid macroscopic phase separation obtaining hybrid materials in the nanoscale range.

### Surface properties

Contact angle measurements with water, performed on dual-cured films, showed an increase in wettability by increasing the TIP content in the photocurable formulation (Fig. 5). In the presence of 30 wt % TIP, the contact angle approaches  $30^\circ$  and it remains practically unchanged by further increasing the TIP content in the photocurable formulation. It is possible to suppose that above 30 wt % TIP saturates the film surface. Contact angle measurements were repeated after many days and this hydrophilicity effect was maintained.

### CONCLUSIONS

Titanium dioxide containing hybrid nanocomposite coatings were prepared by a dual-cure process, which involves first the photopolymerization of acrylic double bonds and then hydrolysis and subsequent condensation of alkyltitanate groups.



**Figure 5** Wettability trend (water contact angles) of the film surface as a function of TIP concentration.

Large amount (above 30 wt %) of the inorganic phase precursor, titanium TIP, prevents a complete acrylic double bond conversion due to a competition of UV light absorption between the photoinitiator and the formed  $\text{TiO}_2$  particles, however, after the condensation step gel contents still above 80% are achieved.

AFM analysis gave evidence of a strong interaction between the organic and inorganic phases, with the formation of titania domains in the nanoscale range; this was possible thanks to the hydroxyl-ethyl-acrylate employed as coupling agent. A high- and long-term stable hydrophilic surface is induced in the presence of 30 wt % of titanium isopropoxide and was attributed to a  $\text{TiO}_2$  surface segregation

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