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ORIGINAL CONTRIBUTION

Novel strategy for tailoring of SiO_2 and TiO_2 nanoparticle surfaces with poly(ε-caprolactone)

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Abstract A novel strategy was developed for tailoring of SiO_2 and TiO_2 nanoparticle surfaces with poly(ε-caprolactone) (PCL). Thus, a self-curable polyester, poly(2-hydroxypropylene maleate) was adsorbed on the nanoparticle surfaces and heated to 180°C to give a cross-linked polyester layer with residual hydroxyalkyl groups on their surfaces. Surface-initiated polymerization of ε-caprolactone from hydroxyalkyl groups on the surfaces yielded core-shell nanoparticles with cross-linked core and PCL shells (22.2–71.4%). The organic shell layers around the nanoparticle cores were evidenced by transmission electron microscopy, dynamic light scattering, and thermogravimetric analyses techniques. The core-shell nanoparticles were then employed in preparing the stable and the homogenous dispersions with poly(methyl methacrylate-*stat*-butyl acrylate) solutions. An application of the solutions onto glass substrates yielded uniform and nearly transparent free standing films (40–60 μm) with good homogeneity as inferred from scanning electron microscopy pictures.

Keywords Nanoparticle · Surface-initiated polymerization · Poly(ε-caprolactone) · Adsorption · Surface modification · Unsaturated polyester

Introduction

Organic–inorganic hybrids incorporating nanosize inorganic fillers are the focus of intense research activities to their unusual optical, electrical, and mechanical properties originating from large surface area to volume ratio and finite size effects [1]. Surface modification of inorganic nanoparticles is essential for the fine dispersion in organic and polymeric matrices. Attachment of polymers onto surfaces of nanoparticles is mostly the preferred way of their surface modification. Beside traditional sol–gel technique [2], in situ polymerization [3, 4], grafting onto [5], grafting from [6–8], and grafting through [9, 10] polymerization techniques have been widely employed for surface modification of nanosize particles. Among those, the "grafting from" technique has proven valuable in creating polymer brushes on solid surfaces. Polymerization from the initiator groups on solid surfaces is also termed as "surface initiated polymerization" (SIP). Since the pioneering work of Prucker and Ruhe [11, 12], SIP technique has been widely employed for tailoring of planar, spherical, or amorphous surfaces with polymer brushes [13, 14]. Comparing with the ionic initiation, radical initiation is a most widely studied strategy to form polymer brushes on silica surfaces due to simplicity and versatility of the latter.

Controlled radical polymerization processes, namely atom transfer radical polymerization [15, 16], nitroxide-mediated radical polymerization [17], and reversible addition–fragmentation chain transfer processes [18], have been employed successfully in the SIP of various monomers from metal, pigment, and semiconductor nanoparticles. An alternative approach for decoration of nanoparticle surfaces with polymers is ring-opening polymerization (ROP) of some cyclic esters, e.g., ε-caprolactone. ROP of ε-caprolactone has been reported by Dubois and his coworkers, in which the

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cyclic ester monomer was polymerized in living fashion through amine-terminated silane coupling agent on the surfaces of silica nanoparticles using trialkyl aluminum as initiator [18].

One key issue in SIP strategy is immobilization of initiator groups onto the particle surfaces for application of the “grafting from” technique. However, there is yet no general recipe applicable to every particle surface for immobilization of the initiating groups, and the modification of each surface essentially needs different individual chemical processes. For instance, a common way of introducing initiator groups onto silica surface is the modification with silane coupling agents. Numerous silane coupling agents with amine, halogen, or vinyl residues have been developed for modification of silica surfaces [19]. However, the silane coupling agents are almost limited to silica surfaces, and they cannot be used for incorporation of the initiating sites onto a wider selection of other particle surfaces.

In this work, we report a general strategy for incorporation of hydroxy groups onto the surface of SiO_2 and TiO_2 nanoparticles for the ROP of ε-caprolactone from their surfaces. This strategy relies upon adsorption of self-curable polyester [20], poly(2-hydroxypropylene maleate), on the nanospheres from acetone solution, which is followed by curing at 180 °C to give cross-linked capsules with residual hydroxy groups on their surfaces. The ROP of ε-caprolactone can be initiated from residual hydroxy groups of poly(2-hydroxypropylene maleate) (PHPM) to yield highly dense poly(ε-caprolactone) (PCL) grafts on the nanopowder surfaces.

Experimental

Materials

Glycidol (Acros, 96%) was distilled under reduced pressure before use. This purification is essential since the commercial product slowly polymerizes upon standing. Maleic anhydride (E. Merck, >99%), TiO_2 nanopowders with 25–70 nm of average particle size and 20–25 $m^2\ g^{-1}$ of BET surface area (Aldrich), and fumed silica with 200±25 $m^2\ g^{-1}$ of BET surface area (Aldrich) were used as purchased. Poly(methyl methacrylate-*stat*-butyl acrylate) was purchased from BASF in aqueous emulsion (60% solid content). The copolymer was isolated by precipitation in acidified aqueous solution. The dried copolymer was soluble in acetone, toluene, and tetrahydrofuran (THF). ε-Caprolactone (Aldrich 99%) was distilled over CaH_2 under vacuum. Dimethoxyethane (Acros) was distilled over metallic sodium before use. Micropowders of SiO_2 (E. Merck) and TiO_2 (E. Merck) were also used to examine adsorption of the self-curable polyester on their surfaces. Tin(II) 2-ethylhexanoate (Sigma, 95%) was used as received.

Instrumentation

Thermogravimetric analyses (TGA) were performed by Perkin Elmer instruments Diamond TG/DTA Analyzer, with a heating rate of 10 °C/min under air atmosphere. Fourier transform infrared (FT-IR) spectra were recorded with a Perkin Elmer FT-IR Spectrum One B spectrometer. Transmission electron microscopy (TEM) images were obtained by HR TEM, JEOL JEM 2100. Scanning electron microscopy (SEM) pictures of the composite films were taken by JEOL JSM 6335 F using field emission. Sonications were carried out with a Bandelin Sonopuls HD 3200 homogenizer at 20 KHz (at 40% power out), using MS 72 probe. The crystal structures of the as-prepared SiO_2 and TiO_2 nanoparticles were examined by X-ray diffraction (XRD) using a D/max-γA diffractometer (Cu K_α radiation) at a scanning rate of $10° \mathrm{min}^{-1}$ in the diffraction angle range $2\theta=10$–$90°$. The hydrodynamic diameters of nanoparticles in each step were measured by dynamic light scattering (DLS; NanoS, Malvern Instruments, London, UK) in acetone medium (1% (*w*/*w*)). DLS was applied with an angle of 170° by using He–Ne laser (4 mW) operated at 633 nm.

Adsorption of the polyester on the nanoparticle surfaces and its curing

Encapsulation of the nanopowders was achieved by surface adsorption of PHPM from acetone solution and followed curing as described for the microparticles (see Online Resource). The nanopowder samples (6 g) were mixed with acetone solution (20 mL) of PHPM (22.3% *w*/*w*) and stirred for 15 min. Thereafter, acetone was removed by rotary evaporator, and the residue was heated at 180 °C for 30 min for cross-linking of the polyester adsorbed.

Surface-initiated polymerization of ε-caprolactone from the nanoparticle surfaces

The cured sample (5 g), 16 mL of redistilled ε-caprolactone (0.144 mol), and 10 mL dimethoxyethane were charged in a 100-mL flask after five times of empty–fill cycles with dry nitrogen. To the mixture, 0.2 mL of tin(II) 2-ethylhexanoate was added with a hypodermic syringe while stirring, and the temperature of the bath was adjusted to 110 °C. The reaction was continued for 8 h at this temperature. The mixture was cooled and precipitated in 100 mL ethanol, filtered, and washed with ethanol (2×30 mL). Then, superficially dried samples were suspended in acetone (40 mL) to remove free PCL. The acetone was removed by centrifugation (3,000 rpm, 5 min). The samples were redispersed in acetone and centrifuged again. The resulting gel-like samples were then dried under vacuum at 50 °C for 6 h and stored in tightly closed bottles. Dry weights were found 6.5 and 6.1 g for the samples with SiO_2 and TiO_2, respectively.

Preparation of polymer nanocomposite films

Commercial (methyl methacrylate-*stat*-butyl acrylate) copolymer (5 g, approximately 50% MMA) was dissolved in 50 mL of acetone. The organically modified nanoparticles (0.5 g) were mixed with 10 mL of the above polymer solution. The mixtures were sonicated at 20 KHz (with 40% power out) for 5 min. The pigment dispersions obtained were stable, and no precipitation or phase separation was observed within 3 days of standing at room temperature. The dispersions were then applied onto polished glass surfaces by means of film maker (Sheen Automatic Film Applicator) to give composite films with 60 μm of wet thickness. The surface films were left to stand under atmospheric pressure for 24 h at room temperature. The films were detached from the glass surfaces by hot water and dried at 40 °C overnight. The free-standing composite films were used for the surface characterizations with SEM.

Results and discussion

Stepwise heating of glycidol–maleic anhydride mixture gave unsaturated polyester (Scheme 1) in moderate molecular weights, as described before [20]. The resulting polyester with hydroxy groups in each repeating unit was demonstrated to be highly adhesive to the various substrates such as glass, metal, or wood and undergoes rapid cross-linking upon curing at 180 °C.

In the present work, this chemistry was employed in coating TiO_2 and SiO_2 nanoparticles with cross-linked polyester, poly(2-hydroxypropylene maleate), for further surface modification with poly(ε-caprolactone). This was carried out in three steps as depicted in Scheme 2. In the first step, the self-curable polyester was adsorbed on the nanoparticle surfaces from acetone solution, which was then cured at 180 °C for 30 min in step 2. This process gave nanoparticles with cross-linked polyester on their surfaces. ROP of ε-caprolactone was initiated from the residual hydroxy groups in the presence of tin(II) 2-ethylhexanoate as catalyst to yield PCL surface grafts in the final step.

In order to inspect adhesion capability of the polyester onto the nanopowders, adsorption experiments were carried out with micropowders of TiO_2 and SiO_2. Experiments revealed that the equilibrium adsorption data obey Langmuir adsorption isotherm. The maximum adsorptions were estimated from the intercepts of the linear $1/q_E$ versus $1/C_E$ plots (Langmuir plots), where q_E and C_E denote the equilibrium adsorption and equilibrium concentration, respectively. The relevant data are collected in Table 1.

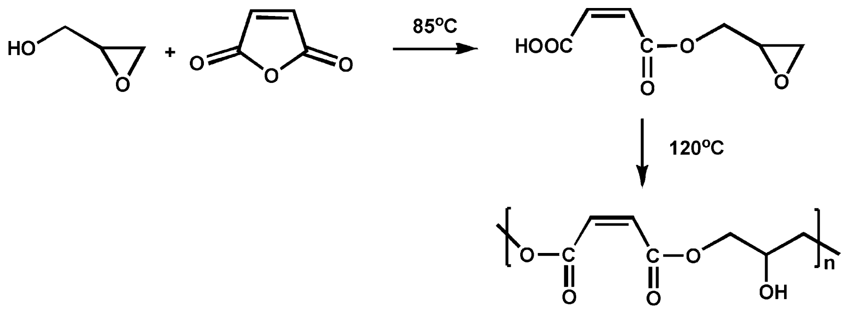
The maximum polyester adsorptions were determined to be 0.246 and 0.281 g per gram of TiO_2 and SiO_2, respectively. These values were also confirmed by TGA of the samples after polyester adsorption from PHPM solutions (3 g/10 mL acetone). The thermograms taken under air atmosphere indicated the presence of 21–21.5% (*w*/*w*) of polymer layer, which decomposes around 390 °C. These values correspond to 0.26 and 0.28 g of organic mass per gram of TiO_2 and SiO_2, respectively.

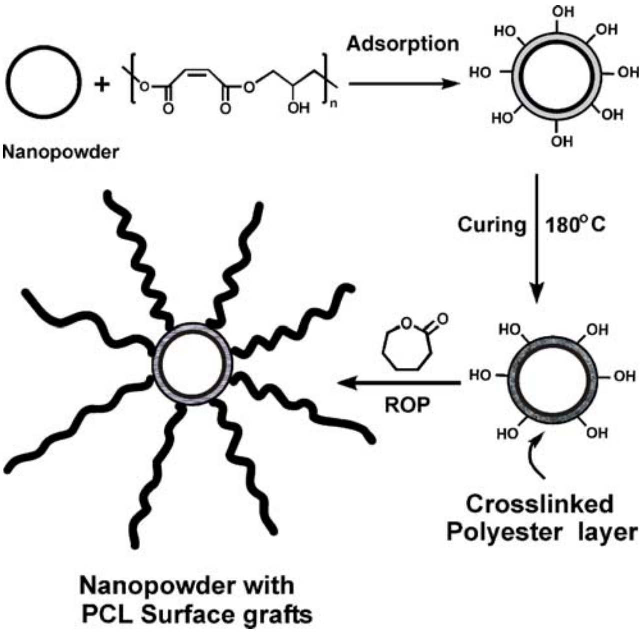
Entrapment of the nanopowders within the cross-linked polyester

The same surface treatment was applied to commercial SiO_2 and TiO_2 nanopowders. This process resulted in encapsulation of the nanoparticles by cross-linked polyester after curing process. Figure 1b shows FT-IR spectrum of the silica sample with adsorbed polyester. In this spectrum, typical ester carbonyl and carbon–carbon double bond vibrations appear at 1,720 and 1,640 cm^{-1}, respectively. Bare silica nanoparticles show no peaks in this region (Fig. 1a). After curing of the sample, intensity of the second peak decreases as shown in Fig. 1c. This implies the addition of the hydroxy groups to the maleate double bonds while cross-linking of the polyester as described before [20].

Extents of cross-linking in the curing process were estimated by comparison of the integral ratios of the two

Scheme 1 Preparation of the self-curable polyester





Scheme 2 General process for tailoring of SiO_2 and TiO_2 nanoparticle surfaces by surface-initiated polymerization of ε-caprolactone

peaks in Fig. 1b and c. The percentage cross-linking of the adsorbed polyester was assigned by the formula:

$$\left(\frac{I^0_{C=C}}{I^0_{C=O}} - \frac{I_{C=C}}{I_{C=O}}\right) / \frac{I^0_{C=C}}{I^0_{C=O}} \times 100$$

where $I_{C=C}$ denotes the integral of the double bond vibration band at 1,640 cm^{-1} for the cured samples, $I_{C=O}$ is the integral of the carbonyl peak at 1,720 cm^{-1} in the IR spectra of the cured samples, and superscript "zero" represents the integrals of the corresponding peaks for noncured samples. This estimation revealed 18.7% of double bond consumption in the cured polyester adsorbed on the SiO_2 nanopowder. Since equal percent of the hydroxy groups were involved in the cross-linking, the powder surface contained residual hydroxy groups (81.3%) and an equal percent of double bonds as well.

Similar comparison of the integral ratios of those peaks in Fig. 2 gave 28.6% double bond consumption in the thermal curing of the polyester adhered to TiO_2 surface. Amounts of polyester that adhered to the nanopowder surfaces were also assigned by TGA of the cured samples.

Table 1 Adsorption of the polyester on microparticle surfaces

Micropowder	Adsorption of the polyester (g/g)[a]	Weight loss of encapsulated pigment (by TGA at 400°C)
TiO_2	0.246	21.5%
SiO_2	0.281	21%

[a] Based on Langmuir plots

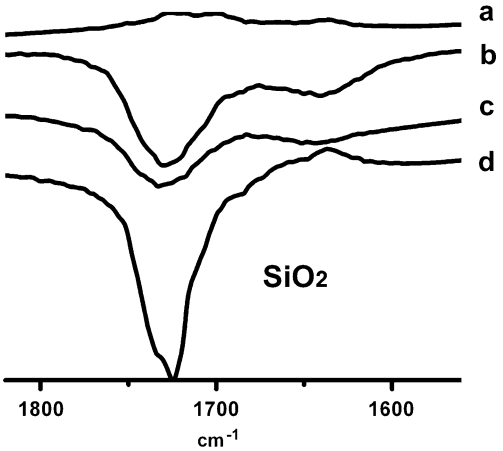


Fig. 1 FT-IR spectra of the fumed silica (**a**), the SiO_2 nanopowder with adsorbed poly(2-hydroxypropylene maleate) (**b**), the SiO_2 nanopowder with cured PHPM capsules (**c**), and encapsulated SiO_2 nanopowder with poly(ε-caprolactone) surface grafts (**d**) in 1,600–1,800-cm^{-1} range

To avoid char formation, the TGA measurements were carried out under air atmosphere. TGA thermograms of encapsulated SiO_2 and TiO_2 nanoparticles (see Online Resource) show that the polyester layer decomposes around 390°C under air atmosphere. For encapsulated silica nanopowders, there occurred an average 2% of weight loss below 200°C originated from humidity. Taking this into consideration, the portion of the cross-linked polyester capsule must be at least 16%, which corresponds to 0.19 g of organic part per gram of the silica particles.

Practically, no weight loss is observed for the case of TiO_2 nanoparticles within 50–200°C. A TGA measurement shows 12% of weight loss for the TiO_2 sample carrying cured polyester at the same heating rate (10°C/min). This implies 0.136 g polyester on the surface of 1 g of the starting TiO_2 nanopowder.

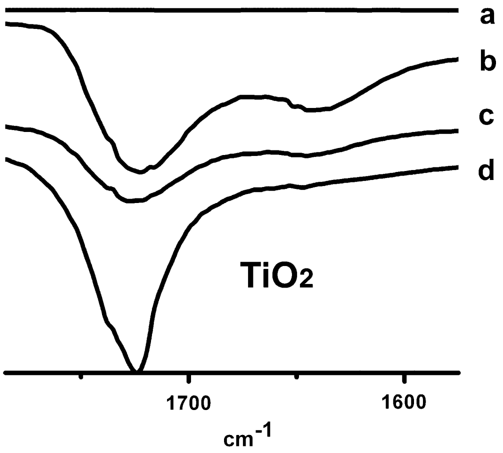


Fig. 2 FT-IR spectra of TiO_2 nanoparticles, naked (**a**), with adsorbed polyester (**b**), with cured polyester capsules (**c**), and with poly(ε-caprolactone) surface grafts (**d**) in 1,600–1,800-cm^{-1} range. Comparison of the spectra in **b** and **c** reveals decreasing intensity of the maleate double bond vibration at 1640 cm^{-1} after curing

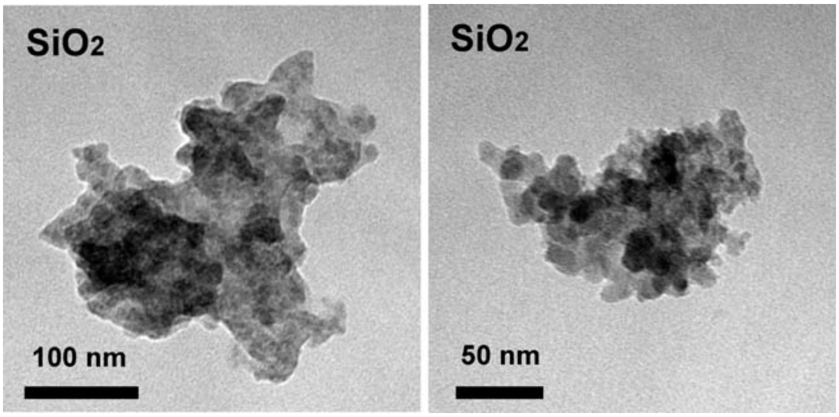


Fig. 3 TEM micrographs of the poly(ε-caprolactone)-shelled SiO_2 nanopowders

XRD patterns of the resulting hybrid particles were the same as those of the virgin nanopowders (see Online Resource). XRD of silica powders, the broad signal at 23° (2θ), indicates amorphous structure of SiO_2 nanopowder in both virgin and cured samples.

Commercial TiO_2 nanopowder shows typical XRD pattern of rutile and anatase (20%) mixture as indicated by the supplier (Aldrich). The TiO_2 sample coated with the cross-linked polyester shows the same XRD pattern. These results indicate that the crystalline structures of the nanopowders did not change in the thermal curing process at 180 °C.

SIP of ε-caprolactone

ε-Caprolactone was polymerized from the surface of the nanoparticles via residual hydroxy groups of the cross-linked polyester, using tin(II) 2-ethylhexanoate as catalyst. Eight hours of the polymerization yielded appreciable quantities of PCL hairy grafts on the nanoparticle surfaces, as inferred from the mass increases (ca. 30% and 22% for the case of SiO_2 and TiO_2 samples, respectively).

The organically modified nanoparticles so obtained were well dispersible in toluene, acetone, and THF.

TEM image of the silica with PCL surface grafts in Fig. 3 represents nonspherical silica nanoparticles with visible organic layers around the particles. The Figure shows that 20–10-nm size of the silica particles are entrapped within polymer stacks of 50–250 nm. Considering with few tents of microns for the sizes of the starting fumed silica (as specified by the supplier, Aldrich), the observed sizes are significantly small.

Most probably, the formation of smaller SiO_2 particles is due to the mechanical disintegration of the starting particles, under sonication during the process. The thickness of the surrounding organic layer seems not uniform; however, it is comparable with the dimensions of the inorganic species.

Similar organic layers are observable also in the TEM micrograph of TiO_2 sample possessing PCL grafts (Fig. 4). The picture on the right hand represents a nearly spherical particle of 100-nm size having organic shell with a thickness of 7–9 nm. Smaller crystallites appeared around this particle imply possible disintegration of the main particle by sonication.

The TEM image on the left hand shows similar small crystallites (15-40 nm) bundled up in the polymer matrix. Thickness of the organic shell in this case is somewhat less,

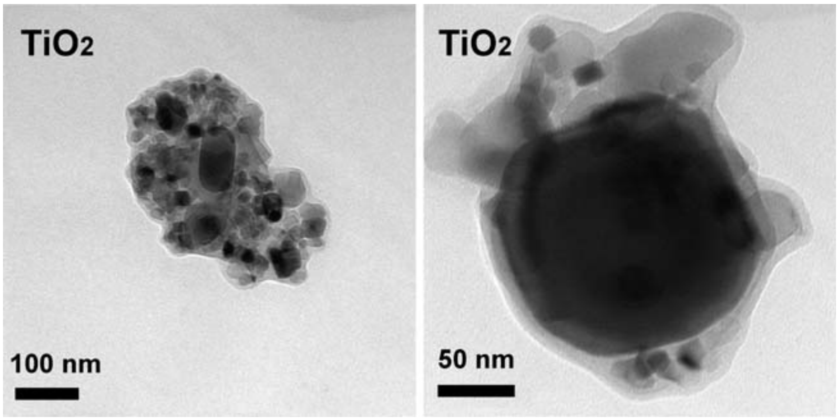


Fig. 4 TEM micrographs of the poly(ε-caprolactone)-shelled TiO_2 nanopowders

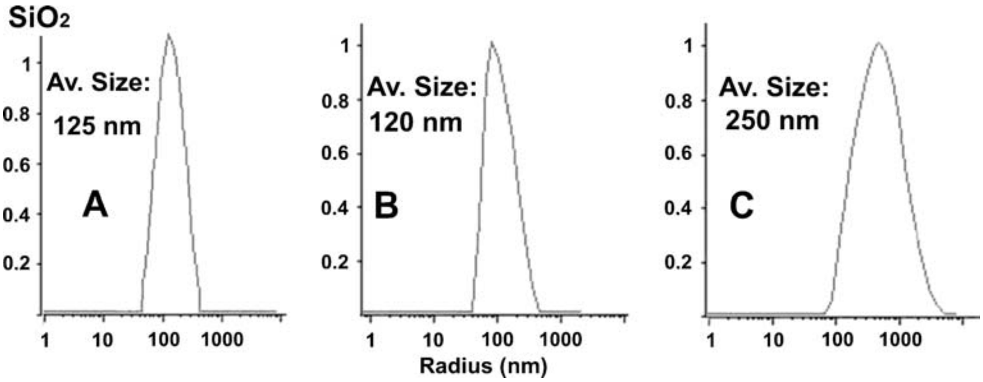


Fig. 5 DLS profiles of the SiO_2 nanoparticles after PHPM adsorption (**a**), cured at 180°C (**b**), and surface grafted with PCL (**c**)

i.e., 7–9 nm, which is consistent with low graft density of PCL (22.2%) for TiO_2 sample. In comparison to the initial size of TiO_2 particles (50–70 nm), their sizes are significantly small (5–20 nm), due to the grinding effect of the sonication as in the case for the silica sample.

In addition, DLS measurements were performed on the particles in order to inspect their size changes by the surface modifications in each step. Figure 5a shows that the silica nanopowders with adsorbed PHPM have an average hydrodynamic diameter of 125 nm. After curing, their average particle size (120 nm) remains almost the same (Fig. 5b). The similarity of the sizes of the particles in both cases might be considered as evidence for nonexistence of further particle growth via interparticle cross-linking by the polyester bridges in the curing process. Significant size growth (250 nm) is observed after graft copolymerization of ε-caprolactone from SiO_2 nanoparticle surface as expected (Fig. 5c). Unimodal DLS curve for the PCL-grafted sample implies absences of the free homopolymer in the product. Taking densities of 1.146 and 2.6 for PCL and SiO_2, respectively, increasing volume per nanoparticle implies 78% percent of grafting which nearly matches with the value assigned from TGA (71.4%). Presumably the difference arises from the solvent, acetone used as dispersing medium for the DLS measurements. Acetone is a good solvent for PCL, and the surface grafts tend to take expanded form rather than globular form in this solvent. Thus, apparent volume of the nanoparticle increases more than that of the expected. These results inferred from DLS are also in consistent with those of TEM pictures described above.

Similar progressive volume increases are observed in DLS of the surface-modified titania samples, as seen in Fig. 6. PHPM adsorbed titania samples showed also unimodal DLS curves indicating nearly narrow size distributions in each step. The average particle size with PHPM adsorbed sample is in 25–30-nm range before and after cross-linking. Hence, volume of the particles does not change practically after the curing process. Absence of significantly larger particles can be ascribed to nonoccurrence of particle growth by inter connection with the polyester adsorbed on the particle surfaces. By introducing PCL surface grafts, their average particle size increases from 30 to 40 nm. Similar estimation based on the final diameter of the particles with titania core revealed a 27.4% (*w/w*) grafting yield, which is slightly greater than that assigned by TGA (22.2%). This result is also fairly consistent with the particle dimensions observed in the TEM images described above. Compared to the size of PCL-grafted silica sample, small increase in the size of

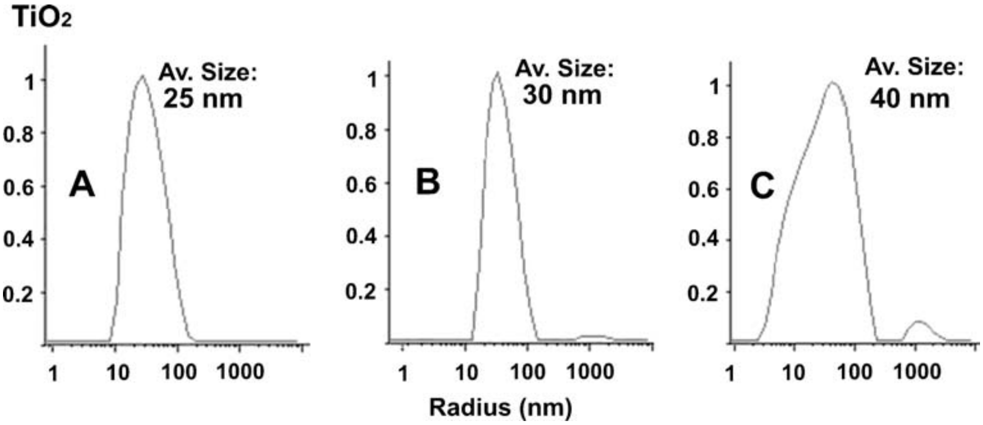


Fig. 6 DLS profiles of the TiO_2 nanoparticles after PHPM adsorption (**a**), cured at 180°C (**b**), and surface grafted with PCL (**c**)

Table 2 Some characteristics of the nanoparticles prior and after grafting with PCL

Characteristics	SiO_2	TiO_2
Hydroxyl group consumption in curing of the PHPM adsorbed on the particle surface[a]	18.7%	28.6%
PHPM content of the cured sample[b]	16%	12%
Total organic content of the particle with PCL surface grafts[b]	51%	28%
ε-Caprolactone-repeating unit per OH-initiating site	8.25	4.0
Percentage grafting of PCL	71.4%	22.2%

[a] Estimated from FT-IR spectra

[b] From TGA

titania is due to the low grafting yield as indicated by TGA measurements.

Avoidance of particle growth by coalescence with the help of surface polyesters must be due to dispersing effect of the sonication and relatively less quantity of the polyester employed for the adsorption. Amount of the polyester (0.223 g per gram) were chosen lower than maximum adsorption capacities (0.281 and 0.246 g/g for SiO_2 and TiO_2, respectively), which were estimated from Langmuir plots (see Table 1). The use of PHPM in less quantity was considered to be crucial to avoid remaining of the nonadsorbed free polyester. Proper selection of the polyester ratio in combination with the sonication must be responsible for preventing undesired particle growth in the encapsulation processes.

TGA of the nanoparticles with silica core and PCL shell indicates 51% of weight loss, which corresponds to 1.04 g of total organic portion per gram of naked silica nanopowder. Since 0.19 g of this quantity comes from PHPM, net weight of the PCL must be 0.85 g per gram of bare silica.

Considering molar mass of the repeating unit of PHPM (172 g mol^{-1}) and 18.7% of hydroxy group consumption in the curing process, the density of the initiating hydroxy groups is calculated to be:

$$\frac{0.19}{172} \times (1 - 0.187) = 9 \times 10^{-4} \mathrm{molg}^{-1}$$

If all the hydroxy groups are assumed to be involved in initiation of the polymerization, the number of ε-caprolactone-repeating units per initiation site would be:

$$\frac{0.85/114}{9 \times 10^{-4}} = 8.25$$

where 114 is the molar mass of ε-caprolactone-repeating unit.

Similar estimation for the core-shell nanoparticles of TiO_2 indicates 0.56 mmol of initiating hydroxyl groups per gram of bare TiO_2. TGA curve of these particles with PCL shells shows 28% mass loss indicating 0.389 g organic portion or 0.253 g PCL per gram of TiO_2. This reveals that four repeating units per hydroxy group take place on the surface. The characteristics are collected in Table 2 for comparison.

In this study, we have not attempted to increase the grafting degrees any further. Since ring-opening polymerization of ε-caprolactone from OH groups is living in nature, the degree of grafting can be increased by continuing the polymerization from the chain ends.

Nanocomposite films

The PCL hybrids of the nanoparticles obtained were used for preparing composite films with commercial poly(methyl methacrylate-*stat*-butyl acrylate) having good film forming and adhesion capabilities. This was performed simply by mixing acetone dispersions of the modified nanoparticles

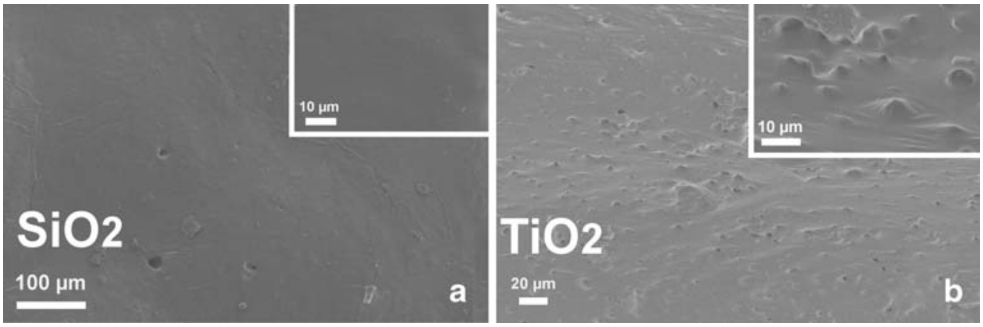


Fig. 7 SEM pictures of free-standing poly(methyl methacrylate-*stat*-butyl acrylate) composite films with SiO_2 (**a**) and TiO_2 (**b**) nanopowders

with acetone solutions of the base polymer, so as final concentration of the nanoparticles to be approximately 15 wt. %. The mixtures were sonicated to give fairly stable and fine dispersions so that no phase separations were observed upon standing for over 6 h at room temperature. The resulting dispersions were applied onto glass substrates by means of standard film maker (60 μm). The obtained dry films on the glass substrates were smooth and nearly transparent.

SEM pictures of the free-standing composite films given in Fig. 7a and b represent homogenous surfaces.

Some solid nanosize dots that appeared on TiO_2 composite films (Fig. 7b) might be due to its less PCL content, in comparison to those of the silica-containing films. Nevertheless, no phase separation is observed in this case as well.

Conclusions

Adsorption of the self-curable polyester PHPM on the SiO_2 and TiO_2 nanopowders and subsequent curing at 180°C yield cross-linked polyester capsules with hydroxy functions on the surfaces. ROP of ε-caprolactone from the residual hydroxy groups leads to the formation of PCL hairy grafts on the nanoparticles. The three-step procedure presented in this paper provides a relatively simple route to PCL-shelled nanoparticles, without using special capping agents for each particle. Although we have studied nanopowders of SiO_2 and TiO_2 in this work, it seems likely that the method is generally applicable for preparing core-shell nanoparticles of various pigments or metals with PCL surface grafts to which PHPM strongly adheres. Homogenous film-forming ability of the resulting particles with poly(methyl methacrylate-*stat*-butyl acrylate) reveals their compatibility with organic host matrixes.

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