Surface Modification of Silica, Titania, and Zinc Oxide Micro Particles with Epoxidized Soybean Oil for Preparation of Polystyrene Composite Films

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ABSTRACT: A novel and convenient procedure is presented for bilayered encapsulation of silica, ZnO, and TiO_2 microparticles using highly adhesive unsaturated polyester, poly (2-hydroxy propylene maleate) (PHM) and epoxidized soybean oil (ESO). Thus, adsorption of PHM onto the particle surfaces from acetone solution (under sonication) and followed curing at 180°C resulted in self crosslinking of the polyester layer by thermally induced addition of its free-hydroxy groups to the maleate double bonds. The adsorption of the polyester onto particle surfaces was demonstrated to obey typical Langmuir isotherms. The oil was tethered onto particle surfaces through residual hydroxy groups of the crosslinked polyester layer at 180°C. Thermo gravimetrical analyses (TGA), FTIR spectra, and transmission electron microscopy (TEM) images of the oil-modified pigments clearly indicated presence of organic layers (26.4–37.3% w/w) with 0.1–0.15 μm thicknesses. The resulting organically modified particles were demonstrated to give fairly stable and homogenous dispersions in concentrated polystyrene solutions. Those dispersions were employed for preparing nearly transparent cast films on glass substrates. Scanning electron microscopy (SEM) images of the freestanding films did not show any phase separation. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 165–171, 2010

Key words: coating; curing of polymers; composites; surface treatment; encapsulation

INTRODUCTION

Preparation of inorganic–organic hybrid materials has been one of the most attracting areas of research due to their application in various fields such as affinity chromatography,[1] composites,[2] coatings, thin films,[3] etc. Compatibility of inorganic materials with organics is crucial for preparing such hybrid materials. Compatibility of inorganic particles is usually achieved by their encapsulation with polymers. Various methods such as sol–gel process,[4] *in situ*-polymerization,[5,6] layer-by-layer assembling,[7,8] and miniemulsion polymerization[9] have been widely employed for encapsulation of micron or nanosize pigments.

Solvent-based chemical methods involve adsorption of polymeric or low-molecular-weight surfactants on the particle surfaces and subsequent crosslinking by physical or chemical means.

Entrapment of micron or nanosize particles within crosslinked polymer matrix and following grafting of functional molecules or polymers onto the particles has been demonstrated to be the most successful strategy for preparing such hybrid composites.[10] Polymerization of vinyl monomers by initiation from colloidal particle surfaces is another alternative to obtain highly compatible pigments.[11,12] One important example of this strategy is attachment of atom transfer radical polymer (ATRP) initiator groups to silica particles and subsequent graft copolymerization to give core-shell particles.[13,14] Disadvantage of this approach is tedious attachment of ATRP initiators onto the particle surfaces before grafting. In addition, substrate dependency of such modification is another limitation of this approach.

Herein, we describe a new and general encapsulation procedure which is applicable to silica, TiO_2, and ZnO microparticles. First step of this procedure involves adsorption of self-curable polyester obtained by reaction of maleic anhydride with glycidol.[15] Having one free hydroxy group in each repeating unit, this polyester is highly adhesive for various substrates such as wood, glass, and metals as described in our previous work.[16]

In this study, this chemistry was employed for encapsulation of the pigment particles, in which the polyester was adsorbed on the particle surfaces and cured to form crosslinked capsules around the microparticles. Epoxidized soybean oil was then anchored to pigment surfaces via residual hydroxyl groups of the unsaturated polyester. The resulting

organically modified pigments were investigated by transmission electron microscopy (TEM), thermogravimetric analyses (TGA), and Fourier transform infrared (FTIR) spectroscopy. These materials were demonstrated to form fairly stable dispersions in toluene solutions of polystyrene. The dispersions so obtained were employed in preparation of polystyrene composite films on glass substrates. Homogeneity of the films was examined by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Glycidol (Acros) was distilled under reduced pressure, before use. This purification is essential since the commercial product slowly polymerizes upon standing. All the other chemicals were analytical grade products: Maleic anhydride (E. Merck), dimethoxyethane (Acros), styrene (Aldrich), epoxidized soybean oil (Akdeniz Kimya, Turkey, with 3.6–3.7 mol epoxy units per mole). They were used as purchased. TiO_2 (Aldrich), SiO_2 (Aldrich), and ZnO (E. Merck) were in powder form. These were sieved and 100–125 μm size ranges of the particles were used in the experiments. Polystyrene used was obtained by radical polymerization of styrene in toluene (35%) using azo bis (isobutyro nitrile), AIBN initiator at 60°C for 4 h. Gel permeation chromatograms (GPC) were taken in THF using polystyrene standards indicated a weight average molecular weight of M_w: 83.000 (M_n: 62.400).

Preparation of poly (2-hydroxy propylene maleate)

This polymer was prepared by stepwise condensation of maleic anhydride with glycidol as reported before.[15] Viscous solution of the polymer (M_n = 13,800) with 10% dimethoxyethane was used in coating applications. The resulting polymer was found to be soluble in ethanol, acetone, dimethylformamide (DMF), tetrahydrofurane (THF); insoluble in benzene, toluene, ether, n-heptane; and slightly soluble in water.

Encapsulation of the pigment particles with polyester

A series of the polyester solutions (7.2–116 gL^{-1} concentrations) were prepared in acetone. Ten milliliters of these solutions were mixed and stirred with 1.0 g of dry pigment powders for 1 h at room temperature. The mixtures were filtered by suction and dried overnight at 70°C under vacuum. The samples were cooled to room temperature and weighed. The adhered quantities per gram of the pigment were

calculated simply by the following relationship: $\frac{(w-w_0)}{w_0}$, where w_0 is initial weight of the pigment sample and w is final weight of the dried pigment after adsorption of the polyester.

Ten grams of each pigment sample was mixed and stirred with 100 mL acetone solution of polyester (116 gL^{-1}) for 1 h as described earlier. The filtered pigment samples were dried at 70°C for 1 h. Then, they were cured at 180°C for 60 min in an oven for thermal crosslinking of the polyesters adsorbed onto the particle surfaces. The samples were cooled to room temperature and weighed. The adsorption data collected were used to build up the adsorption-concentration profiles in Figure 1.

Modification of the particle surfaces with epoxidized soybean oil

Modifications was carried out by reaction of the polyester coated pigments with acetone solution of epoxidized soybean oil as follows: Five grams of the pigment sample was added to the mixture of soybean oil (4 g) and acetone (20 mL) in a 100 mL volume of flask and 0.1 g tributylamine (as catalyst) was added to this mixture. The mixture was stirred for 24 h at room temperature. Acetone was removed under reduced pressure and the residue was heated to 180°C in an oven for 60 min. The residues were cooled, washed with acetone (2 × 30 mL) to remove unreacted epoxidized soybean oil, and then dried under vacuum at 70°C for 24 h.

Preparation of polystyrene-pigment composite films

Ten grams of polystyrene (M_w 83.000) was dissolved in 50 mL of toluene. The oil modified pigment samples (0.3 g) were mixed with 6.4 mL of PS solutions. The mixtures were sonicated at 50 KHz (with 40% power out) for 5 min. The pigment dispersions so obtained were applied onto polish glass surfaces (∼ 5 × 6 cm) by means of filmmaker (Sheen Automatic Film Applicator) to give composite films with 300 μm of wet thickness. The surface films were left to stand under atmospheric pressure for 24 h at room temperature.

To obtain free standing films, the samples were soaked into the hot water (70–80°C) and left to stand for 16 h. The films were peeled out from the glass surfaces with tweezers and dried at 50°C for 4 h at under atmospheric pressure.

The dry samples were used for surface characterization.
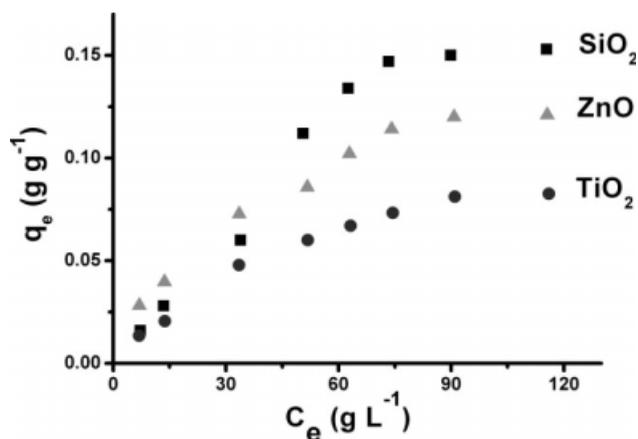
Figure 1 Adsorption of the unsaturated polyester on the pigment powders (125–210 µm); SiO$_2$ (a), ZnO (b), and TiO$_2$ (c). Note that at all concentrations SiO$_2$ surface shows greater equilibrium adsorption comparing with those of the others.

Surface characterization

Thermogravimetric analyses (TGA) were performed by Perkin–Elmer instruments Diamond TG/DTA Analyzer, with a heating rate of 10°C/min under air atmosphere. FTIR spectra were recorded on a Perkin–Elmer FTIR 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.

RESULTS AND DISCUSSION

Encapsulation

Stepwise heating of glycidol-maleic anhydride mixture gives unsaturated polyester (Scheme 1) in moderate molecular weights as described before.[15] As the resulting polyester, poly (2-hydroxy propylene maleate) is thermally curable and highly adhesive for various substrates, it was employed for encapsulation of the micron-size pigments; silica, ZnO, and TiO$_2$.
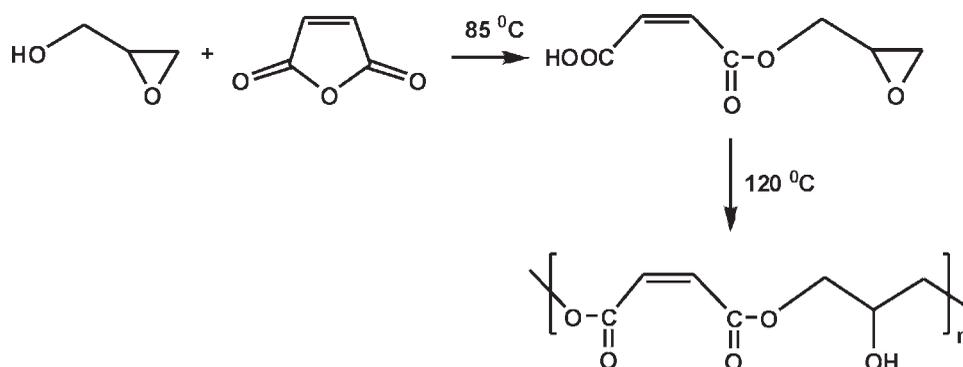
Adhesiveness of the polyester is caused by polar hydroxy group in its repeating units. The encapsulation experiments were carried out simply by adsorption of the polyester from acetone solution and subsequent curing at 180°C. Figure 1 shows the equilibrium adsorption-concentration plots. Adsorption of the polyester follows a typical Langmuir isotherm and levels off at concentrations >75 gL^{-1} (Fig. 1). Neutral silica particles showed greater saturation adsorption (ca. 150 mg per gram). The saturation adsorptions for ZnO and TiO$_2$ are around 120 and 80 mg g^{-1}. Quantitative evaluation of the adsorption data revealed typical Langmuir isotherms in each case.

According to Langmuir isotherm, the equilibrium adsorption is given by;

$$q_e = q_{max} \frac{bC_e}{1 + bC_e}$$

where q_e is the equilibrium adsorption, C_e is concentration at the equilibrium, b is Langmuir constant, and q_{max} is the adsorption capacity. $1/q_e$ versus $1/C_e$ plots (Langmuir plots) were found to be linear (with regression factors $R > 0.99$) from which the adsorption constants were calculated as 3.66×10^{-3}, 3.29×10^{-2}, and 15.85×10^{-2} Lg^{-1} for SiO$_2$, TiO$_2$, and ZnO, respectively.

Adsorption maxima were estimated as 0.615, 0.144, and 0.129 mg per grams of SiO$_2$, TiO$_2$, and ZnO, respectively.

Adhesion of the polyester to the particle surfaces can be ascribed to "a physical adsorption" facilitated by "the hydroxy pendant groups." Although some chemisorptions via carboxyl groups at the chain ends of the polyester might also contribute to adhesion, this effect is of minor importance.

Scheme 1 Preparation of the self-curable polyester, poly (2-hydroxypropylene maleate) by two-step reaction of glycidol with maleic anhydride.
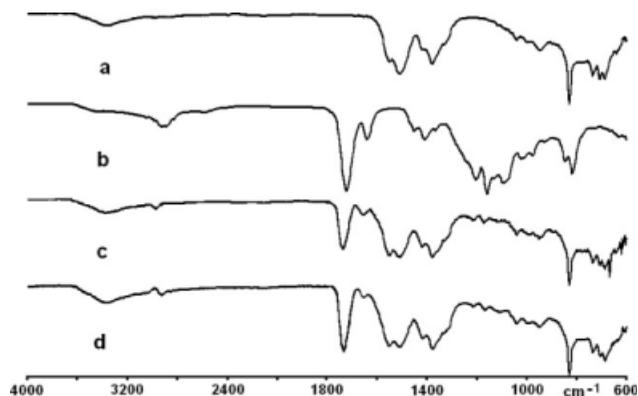
Figure 2 FTIR spectrum of the bare ZnO (a) and free polyester (b). Maleate double bond vibration of the polyester adsorbed (at 1640 cm^{-1}) on ZnO powder decreases significantly after curing at 180°C (c). FTIR spectrum of ZnO sample with oil grafts (d). Intense bands in 1350–1450 cm^{-1} range are due to typical aliphatic C—H bending vibrations of the oil component.

In the case for ZnO, adhesion of polyester via carboxyl end groups is more likely due to its amphoteric nature. As surfaces of SiO$_2$, TiO$_2$, are acidic, chemical sorption of polyester by salt formation with the carboxyl groups seems not to be possible.

The pigment samples so prepared were heated at optimum temperature,[13] 180°C for crosslinking of the polyester adsorbed. This process gave pigment particles entrapped within the crosslinked polyester matrix. FTIR spectrum of dry ZnO sample [Fig. 2(a)] shows stretching and plane bending vibrations of surface OH groups at 3360 and 1510 cm^{-1}, respectively. Figure 2(b) shows typical stretching vibration band of the maleate double bond of the polyester at 1640 cm^{-1} and a carbonyl stretching vibration bond at 1730 cm^{-1}. Stretching vibration of OH group of PHM shows a broad band centered at 3400 cm^{-1}.
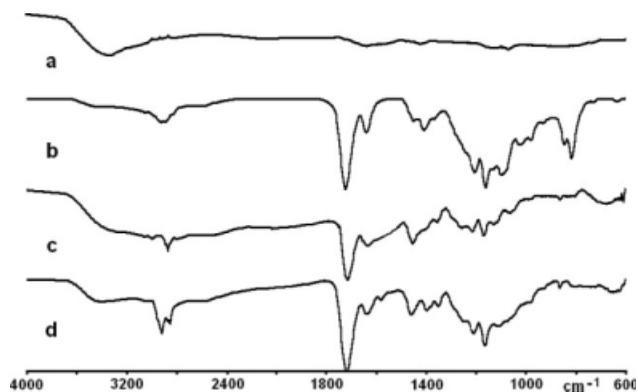
After the curing process intensity of the maleate double bond decreases significantly, whereas intensity of the carbonyl bond vibration at 1730 cm^{-1} remaining almost the same, as shown in Figure 2(c). This implies that the curing process results in addition of the hydroxy groups to the double bonds and crosslinking takes place, as described before.[13]

Therefore, extents of the crosslinking were estimated based on percentage decrease in the intensity ratio of the two bands, using the following relationship;

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

where $I_{C=C}$ denotes integral of the double bond vibration band at 1640 cm^{-1} for the cured samples. $I_{C=O}$ is integral of the carbonyl peak at 1730 cm^{-1} in the IR spectra of the cured samples. The superscript "zero" represents integrals of the corresponding peaks for noncured samples.

This estimation indicated 14.5% double bond consumption in the curing process.

Since equal percent of the hydroxy groups involved in the crosslinking, the pigment surfaces must still contain hydroxy groups (85.5%) and equal percent of the double bonds as well.

Generally, addition of hydroxyl groups to the double bonds is known to be an acid catalyzed reaction. The crosslinking in the present process occurs without acid catalyst at elevated temperature, most probably due to active nature of the double bonds between two carboxyl groups.

Adsorption of the polyester on TiO$_2$ and SiO$_2$ is followed by their FTIR spectra (Figs. 3 and 4). The

Figure 3 FTIR spectrum of the bare TiO$_2$ (a) and free polyester (b). Maleate double bond vibration of the polyester adsorbed (at 1640 cm^{-1}) on TiO$_2$ powder decreases significantly after curing at 180°C (c). FTIR spectrum of TiO$_2$ sample with oil grafts (d). Aliphatic C—H bending vibrations of the oil component show intense bands in 1350–1450 cm^{-1} range.
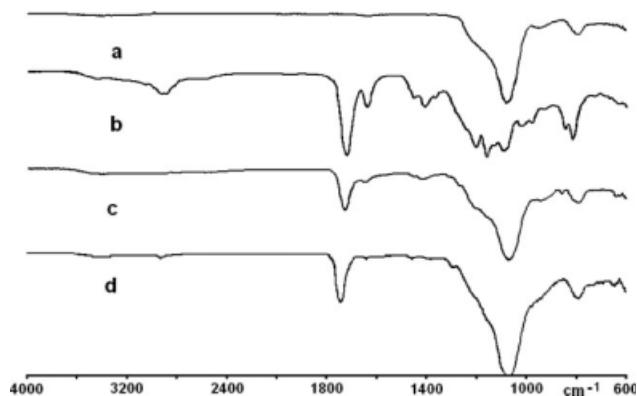
Figure 4 FTIR spectrum of the bare SiO$_2$ (a) and free polyester (b). Maleate double bond vibration of the polyester adsorbed (at 1635 cm^{-1}) on SiO$_2$ powder decreases significantly after curing at 180°C (c). FTIR spectrum of SiO$_2$ sample with oil grafts (d). The intense bands in 1350–1450 cm^{-1} range are associated with typical aliphatic C—H bending vibrations of the oil component.
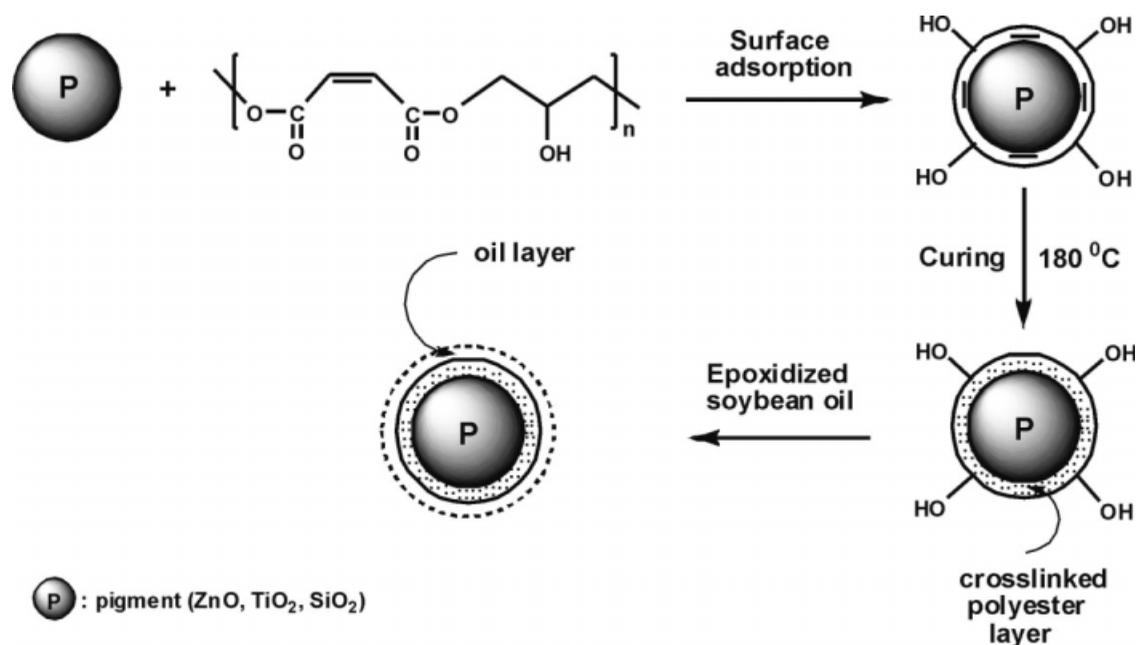
Scheme 2 Schematic illustration for surface modification of the pigment microparticles. The process involves three steps; (i) adsorption of the self-curable polyester on the particle surfaces, (ii) generation of crosslinked polyester capsules around the particles by curing, and (iii) covalent attachment of epoxidized soybean oil onto the surfaces via free hydroxyl groups.

bare TiO_2 shows only one peak [Fig. 3(a)] at 3360 cm^{-1}, which is associated with OH stretching vibration originating from surface TiOH groups. Upon the polyester adsorption and followed curing intensity ratio of the maleate/carbonyl vibration bands decreases similarly, due to crosslinking of the polyester on TiO_2 surfaces.

Similar patterns are observed also in FTIR spectra of the samples with SiO_2 (Fig. 4). Thus, Si—O—Si stretching vibration band of this sample at 1080 cm^{-1} [Fig. 4(a)] is observed also in the spectrum of the polyester coated sample [Fig. 4(c)], together with typical bands of the original polyester. Marked decrease in the intensity of maleate double band vibration at 1635 cm^{-1} reveals consumption of this bond in the curing process.

Surface modification with epoxidized soybean oil

Both hydroxy groups and double bonds can be utilized for further modification of the pigment surfaces. In this work, the residual hydroxy groups were used for the surface modification with epoxidized soybean oil. Commercial epoxidized soybean oil with average 3.6 mol oxirane units per mole was employed for modification of polyester-coated pigment samples in combination with tributylamine as catalyst (Scheme 2).

Attachment of the oil molecule to the surface takes place through hydroxy groups on the crosslinked polyester capsule by ring opening of the oxirane units. As bonding of an epoxy group with the hydroxy group on the surface generates a new hydroxy group, logically amount of oil tethered to the surface would be unlimited. For this reason, we have study to increase the oil contents any further. The overall process can be considered as polymerization epoxy groups of soybean oil through hydroxyl groups on the surfaces. The two-step process followed gave encapsulated pigments with bilayer shells as depicted in Scheme 2.

TGA of the polyester-coated samples obtained in the first step (Table I) indicated 8.5–16% (w/w) of polyester layers decomposed around 390°C. These

TABLE I
TGA Results of the Polyester Encapsulated and Oil-Modified Pigments

Pigment	Adsorption of the polyester (g/g)	Decomposition temp. of organic layer (°C)	Weight loss of encapsulated pigment (%)	Weight loss of oil-modified pigment (%)
ZnO	0.118	390	11.2	31.5
TiO_2	0.081	385	0.08	26.4
SiO_2	0.150	390	14.0	37.3
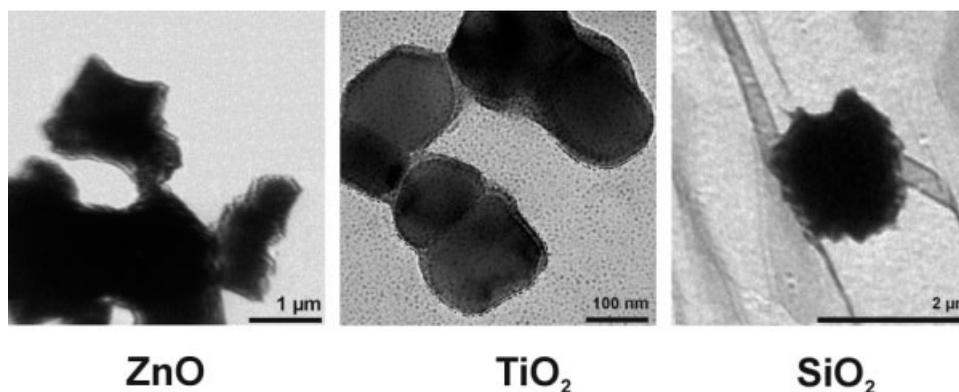
Figure 5 TEM images of the pigments with oil modified surfaces. Note that there is no free polymer or organic substances remaining nonadhered between the pigment particles. The light shadows at the edges of the islands must be due the organic layers. Continuity of these layers can be ascribed to homogeneity of the organic capsules around the particles of ZnO (left), TiO$_2$ (middle), and SiO$_2$ (right).

values imply 0.085–0.16 g mass increases per grams of the fresh pigments in the polyester coating process.

These quantities are in consistent with the results obtained from adsorption measurements. The TGA curves of the samples with oil surfaces represent reasonably high organic contents (26.4–37.3%).

These quantities correspond to 0.359–0.595 g of total organic shell layer per grams of the naked pigment particles. By subtracting the polyester contents, masses of the oil layers were found to be 0.342, 0.279, and 0.445 g per grams of initial ZnO, TiO$_2$, and SiO$_2$, respectively. In addition, FTIR spectra of the organically modified pigments indicate presence of organic materials in their structures. Figure 2(c,d) show FTIR spectra of ZnO particles with polyester and oil shells as representative examples. In Figure 2(c), the peaks appeared at 1730 and 1640 cm^{-1} are associated with carbonyl and double bond vibrations of maleate component of the polyester coating on ZnO powders. As some percent of the double bonds has been consumed in the previous curing process, the later is observed as weak band. After incorporation of soybean oil, these bands become relatively less intense [Fig. 2(d)] and C—H plane bending

vibration bands of the aliphatic groups in 1350–1450 cm^{-1} range become stronger. This is evidence for the presence of surface tethered oil molecules on the particle.

The increasing intensity of carbonyl vibration bands in 1715–1720 cm^{-1} range in Figures 3(d) and 4(d) clearly implies incorporation of soybean oil onto surfaces of the TiO$_2$ and SiO$_2$ particles.

As a result, the process presented allows surface modification of those pigment particles with considerable amounts of soybean oil.

TEM images of the resulting pigments are shown in Figure 5. To obtain better contrasts, the images represented in this figure were selected from smaller particles. "This figure shows organic layers with an average thickness of 0.1–0.15 μm as seen at the visible edges of the particles. The images in this figure can be ascribed to complete encapsulation of the particle surfaces by the polyester, which is crucial for preparing composite films."

The composite films

The encapsulated pigments so obtained were used for preparing polystyrene composite films. This was
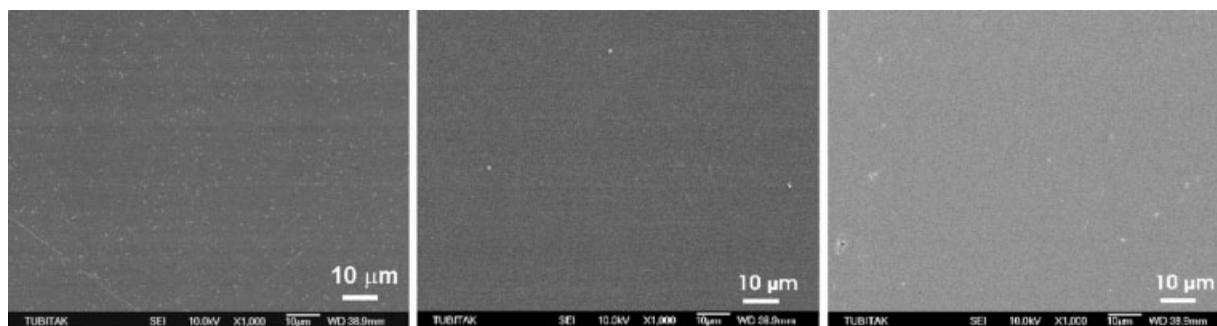
Figure 6 SEM pictures of the composite films constituting with PS-ZnO (left), PS-TiO$_2$ (middle), and PS-SiO$_2$ (right). Homogenous appearance of the surfaces implies nonexistence of phase separation in the mixtures with the base polymer, polystyrene.

performed simply by mixing of modified pigment samples with polystyrene solutions (10 g in 50 mL toluene). The dispersions obtained by sonication were stable and no phase separations were observed upon standing for 6 h.

The resulting dispersions were applied onto glass substrates by means of standard filmmaker (300 µm). The cast films removed from the glass surfaces nearly transparent and highly robust sheets. SEM pictures of the freestanding films with 13–16% pigment contents in Figure 6 represent homogenous and smooth surfaces indicating excellent compatibility of the organically modified pigment particles with the polystyrene matrix.

CONCLUSIONS

Adsorption of the self-curable polyester on the surfaces of the pigment powders (TiO_2, ZnO, and SiO_2) and thermal curing at 180°C results in encapsulation of the microparticles with crosslinked polyester. Followed reaction of the microparticles with epoxidized soybean oil generates an oily shell layer by surface-initiated ring opening of the epoxy groups. Percentage of the oily graft so obtained might be as high as 44.5% for SiO_2, depending on the process conditions.

The method presented offers a general pathway for surface modification of the pigment particles. It was demonstrated that such an oil modification provides excellent compatibility with polystyrene. Although the pigments studied were TiO_2, ZnO, and SiO_2, it seems likely that the method applicable for all pigments in micron or nanometer-sizes. Of course, detailed works dealing with optimization of the mechanical properties of the freestanding films

as a function of variables such as percentage solid content, oil to pigment ratio, and particle size remain to be studied. However, this general method is promising and may provide an easy access to many inorganic–organic hybrids, which are difficult to obtain by other means. In addition, application of the procedure to nanosize metal or semiconductor particles would be of interest in preparing permanently stable nanoparticle dispersions.

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