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Dedicated to Dr. Maria Zaharescu
on the occasion of her 80th anniversary

WATER-REPELLENT GLASS BY HYDROPHOBICALLY MODIFIED POLY(ACRYLATE)-SURFACTANT COMPLEXES AND SILICA

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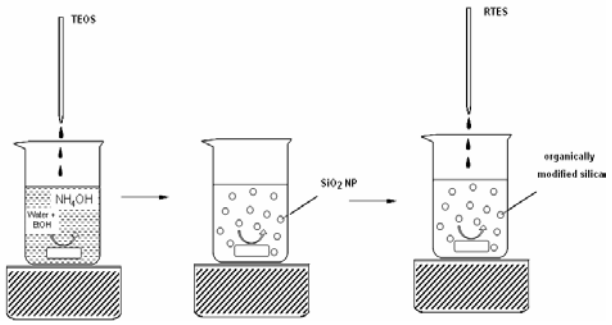
The present work investigates the influence of silica nanoparticles upon the wettability properties of hydrophobically modified poly(acrylate)-surfactant – silica films. The organic-inorganic films were obtained via layer-by-layer method. The silica nanoparticles were synthesized by a sol-gel method using the Stöber process with tetraethoxysilane (TEOS) and alkyltriethoxysilane (RTES). The size of silica nanoparticles was measured by dynamic light scattering (DLS) and environmental scanning electron microscopy (ESEM). The functionalization of silica nanoparticles was confirmed by Fourier transform infrared spectroscopy (FTIR). The experimental data show that the hydrophobically modified-poly(acrylate)-surfactant – silica films have a higher contact angle than those without silica nanoparticles.



INTRODUCTION

One of the most important properties of surface is the wettability.[1-4] The water repellent property is related to the roughness and chemical composition of the surface.[5-6] Hydrophobic surfaces have been obtained by sol-gel,[7-10] chemical[11], electrochemical[12] and layer-by-layer method.[13-14] However, the most used technique to obtain hydrophobic surfaces is the sol-gel process because it creates roughness morphology. The obtained new materials have potential in various applications such as automobile glass, building materials, bathroom mirrors and antibacterial surfaces.[15-20]

The present work investigates the morphology and surface properties of the films containing hydrophobically modified poly(acrylates)-cationic surfactant complexes and silica. These hybrid materials are prepared via a sol-gel method with triethoxysilane (TEOS) as precursor and alkyltrietoxysilane (RTES, R = methyl and vinyl) as modifying siloxane. The experiments are carried

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out in water-ethanol mixtures, in the presence of ammonia aqueous solution. The polyelectrolyte-silica films were obtained via electrostatic layer-by-layer technique. The morphology and nanostructure of the silica nanoparticles were studied by dynamic light scattering (DLS), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR-ATR). The morphological properties of the polyelectrolyte-silica films were explored using SEM and atomic force microscopy (AFM). The wetting properties of the prepared films were obtained using the contact angle measurement. The results show an enhancement of contact angle if silica nanoparticles are present into the hydrophobically modified-poly(acrylate)-surfactant – silica films.

RESULTS AND DISCUSSION

Structure, size and morphology of silica particles

In the present work, the modified silica was synthesized by a sol-gel process at a temperature of 60 °C. To confirm the reaction of TEOS with RTES, the hybrid silica obtained during the synthesis was characterized by ATR-FTIR spectroscopy.

Fig. 1 is shown the FT-IR spectra for silica nanoparticles obtained by sol-gel hydrolysis of TEOS and derivatized with MTES and VTES. For both silica hybrids, the ATR-FTIR spectrum has a strong peak at 1030cm^{-1} which belongs to the asymmetric Si-O-Si vibrational modes of the siloxane (Si-O-Si) groups. Another two significant peaks of silica appear at about 771 cm^{-1} associated with the symmetric stretching mode of Si-O-Si groups, and at 879 cm^{-1} due to the Si-OH bonds.[21,22] In Fig. 1a, there is a distinct peak at 1457 cm^{-1} assigned to the CH=CH groups from the modified siloxane. These data attest formation of silica network in hybrids and confirms a result that was previously observed.[23,24]

The silica particles formed via the base-catalyzed hydrolysis of TEOS have a large size distribution with an average diameter (D) of 40 nm (see Fig 2a), and a lower polydispersity index (PdI = 0.2). When the VTES was used in the synthesis of SiONp hybrids, the size of nanoparticles was higher (see Fig. 2b). The polydispersity was larger being reflected by the higher polydispersity index (PdI = 0.5) and an average diameter of 600 nm.

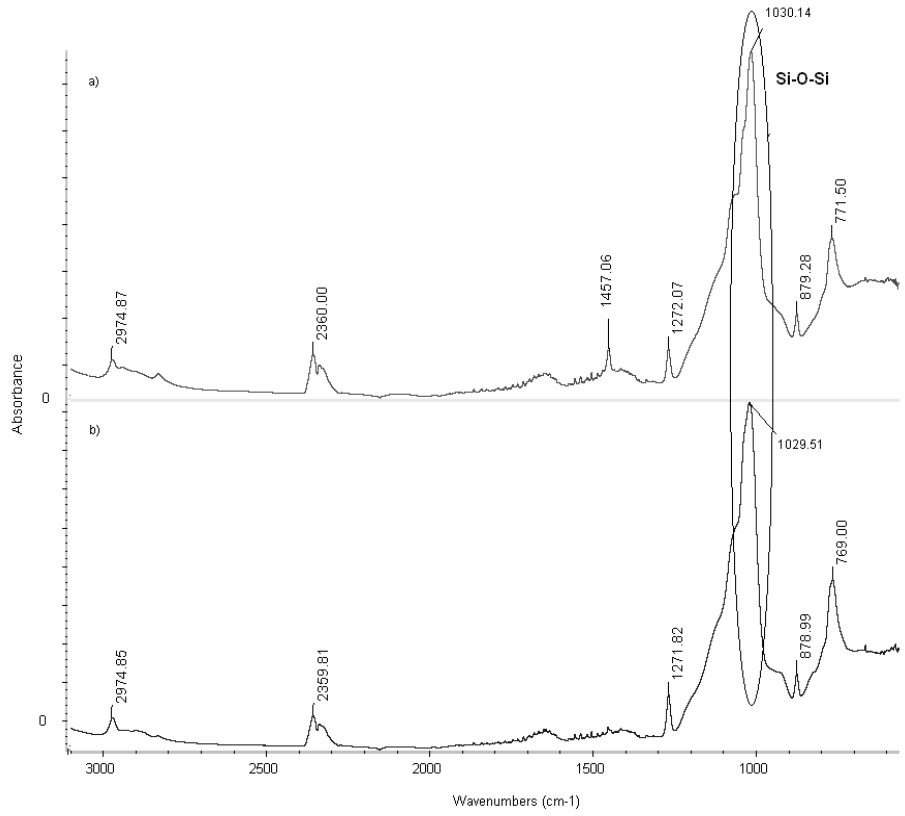

Fig. 1 – FT-IR spectra of silica nanoparticles with TEOS + VTES (a) and silica nanoparticles with TEOS + MTES (b) (dried at room temperature).

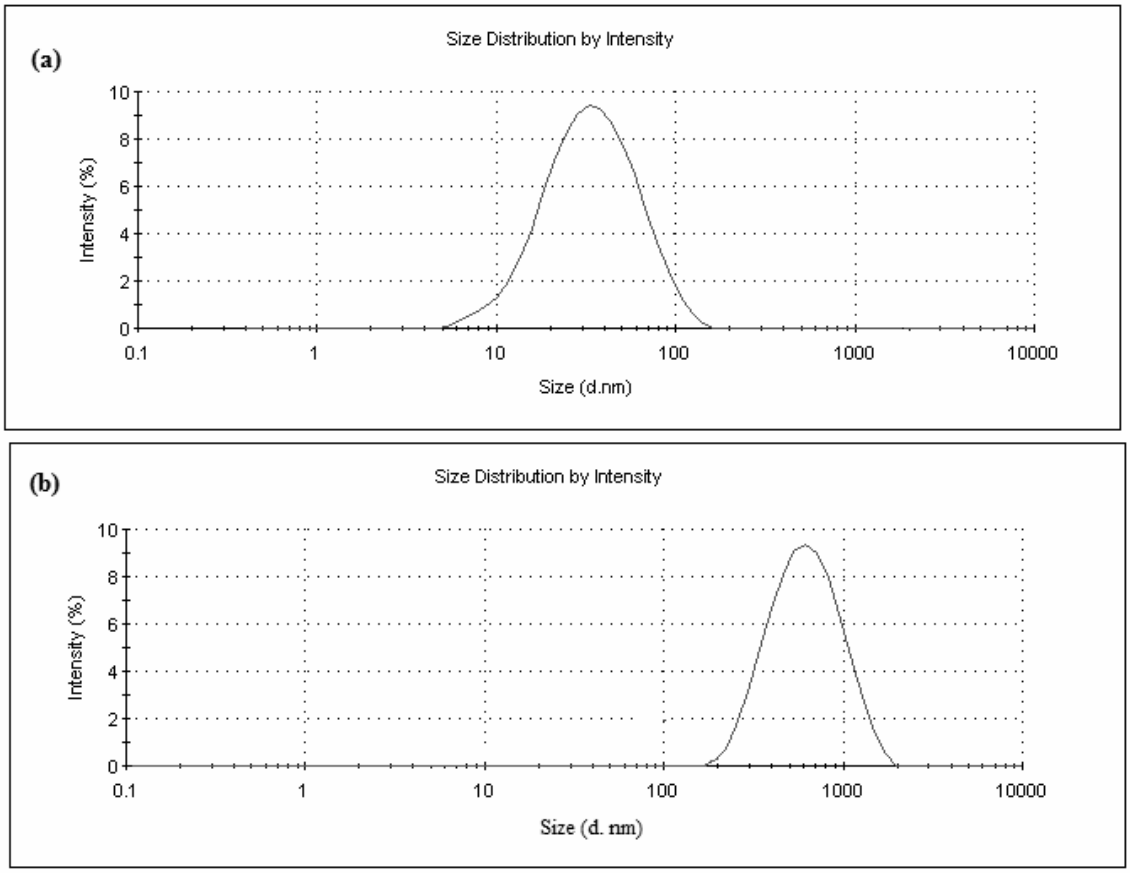

Fig. 2 – Size distribution of SiONp (a) and SiONp-VTES (b).

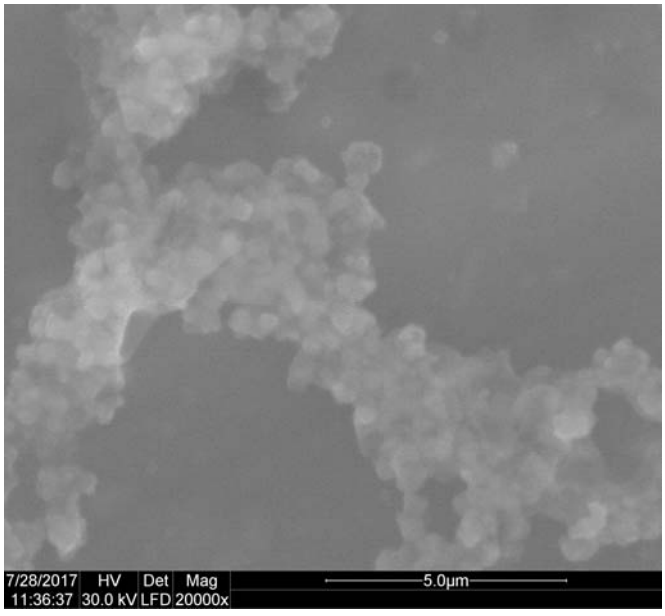

Fig. 3 – ESEM images of silica hybrid with VTES.

It is also possible to observe if the modified silica is polydisperse by ESEM investigation. The ESEM images of hybrid silica obtained are given in Fig. 3. In the case of sample with VTES, the silica nanoparticles are aggregated into a consistent organic medium. These observations explain the results obtained through DLS measurements, showing that the average diameter of the VTES sample is not for a single particle, but for aggregates.

Influence of functionalized silica on the wettability of hydrophobically modified poly(acrylate)-surfactant complexes

The polyelectrolyte-silica films were investigated in order to observe the effect of silica nanoparticles (SiONp) on wettability. The data for PAC_nNa-C_xTAB/PDADMAC without silica nanoparticles were presented in our previous work.[25] Fig. 4 shows the contact angle values for the ($PAC_{18}Na$-$C_{10}TAB$-SiONp-MTES/PDADMAC)$_1$ (Fig. 4a), ($PAC_{18}Na$-$C_{18}TAB$-SiONp-MTES/PDADMAC)$_1$ (Fig 4b), ($PAC_{18}Na$-$C_{10}TAB$-SiONp-VTES/PDADMAC)$_1$ (Fig. 4c) and ($PAC_{18}Na$-$C_{18}TAB$-SiONp-VTES/PDADMAC)$_1$ (Fig 4d). The data show a higher contact angle for films containing silica nanoparticles than without it. For example, the contact angle for ($PAC_{18}Na$-$C_{10}TAB$/PDADMAC)$_1$ without silica is 64º, meanwhile the CA for the ($PAC_{18}Na$-$C_{10}TAB$/PDADMAC)$_1$ with silica nanoparticles with MTES is 74º. The contact angle for the ($PAC_{18}Na$-$C_{18}TAB$/PDADMAC)$_1$ film increases from 70º to 84º if the films contain SiONp-MTES nanoparticles. Conversely, the nature of silica nanoparticles has a critical influence upon the wettability. The experimental data show that the films containing SiONp-VTES has the highest contact angle than those with MTES as a precursor. For example, the CA for ($PAC_{18}Na$-$C_{10}TAB$-SiONp-MTES/PDADMAC)$_1$ is 87º whereas for the ($PAC_{18}Na$-$C_{18}TAB$-SiONp-VTES/PDADMAC)$_1$ is 96º.

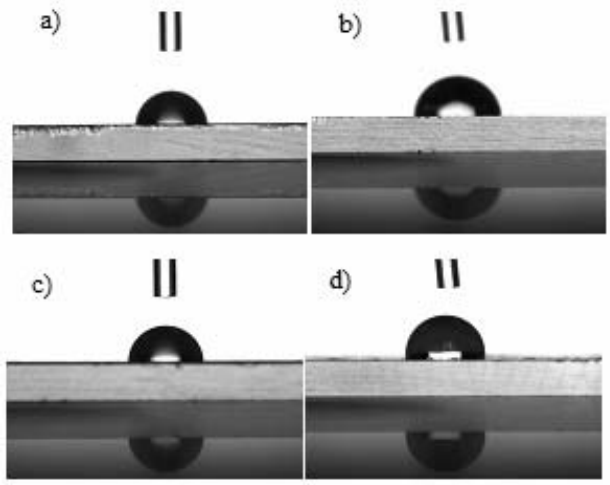

Fig. 4 – Contact angle of the polyelectrolyte-silica films: a) ($PAC_{18}Na$-$C_{10}TAB$-SiONp-MTES/PDADMAC)$_1$, b) ($PAC_{18}Na$-$C_{18}TAB$-SiONp-MTES/PDADMAC)$_1$, c) ($PAC_{18}Na$-$C_{10}TAB$-SiONp-VTES/PDADMAC)$_1$ and d) ($PAC_{18}Na$-$C_{18}TAB$-SiONp-VTES/PDADMAC)$_1$.

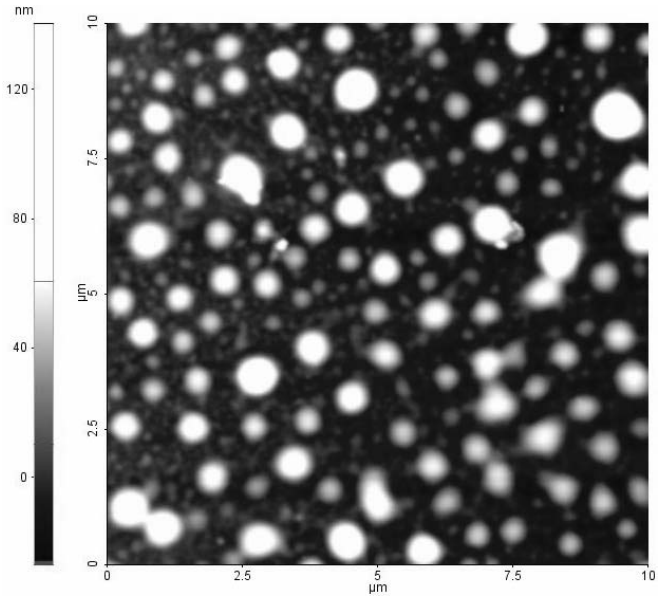

Fig. 5 – AFM image of ($PAC_{18}Na$-$C_{18}TAB$-SiONp-VTES/PDADMAC)$_1$.

In our previous articles[25, 26] we observed that the polyelectrolyte-surfactant complex multilayer films present an uniform morphology consisting in hills and valleys, which have a root mean square roughness from 5 nm for $(PAC_{18}Na\text{-}C_{10}TAB/PDADMAC)_1$ films to 14 nm for $(PAC_{18}Na\text{-}C_{18}TAB/PDADMAC)_1$. The surface morphology for $(PAC_{18}Na\text{-}C_{18}TAB\text{-}SiONp\text{-}VTES/PDADMAC)_1$ is also uniform of hills and valleys, with a RMS roughness around 26 nm (Fig. 5). By comparing the polyelectrolyte-silica films with the films without silica[25], the experimental data show that the contact angle and the surface morphology of the polyelectrolyte-silica multilayer films are higher than those without silica hybrids.

EXPERIMENTAL

Materials

Decyltrimethylammonium bromide ($C_{10}TAB$) (98%), and octadecyl trimethylammonium bromide ($C_{18}TAB$) (97%) were Fluka products. Poly(ethylenimine) (PEI) aqueous solution (50 wt.%) with M_w = 75000, and poly(diallyldimethylammonium chloride) (PDADMAC) aqueous solution (23 wt.%) with M_w 100000-200000 were supplied by Sigma-Aldrich.

Hydrophobically modified sodium polyacrylates, PAC_nNa (n = 18) were obtained by reacting the PAA with octadecylamine after a procedure originally proposed by Iliopoulos.[27] The hydrophobically modified poly(acrylic acid) was characterized by FTIR and ^1H NMR[28] and the grafting degree was of 3 moles %.

Tetraethylorthosilicate (TEOS, 99%), absolute ethanol (99.9%) and hydrochloric acid (37%) were purchased from Merck Company. Methyltriethoxysilane (MTES 99%) and vinyltriethoxysilane (VTES, 97%) were supplied by Sigma-Aldrich.

Synthesis of silica

SiO_2 nanoparticles were prepared via the hydrolysis of TEOS (as a precursor) in the presence of a catalyst, ammonia (NH_4OH) and ethanol as the solvent at room temperature. The molar ratios used in the synthesis were TEOS:EtOH:H2O:NH_4OH = 1:40:4:0.002. After stirring for 4 h, the colloidal solution was ready for use in multilayer films.

Synthesis of the R-trietoxisilane-hybrid silica nanoparticle

The hybrid silica was synthesized by the base-catalyzed hydrolysis and sol-gel condensation (see Fig. 6). In a typical preparation, TEOS (0.4 mol) and ammonia were mixed with 20 mL of ethanol. The formed suspension was magnetically stirred at 60 C for 1/2h, resulting in coloidal silica. The organic–inorganic hybrid silica was syntesized by adition of alkyltriethoxysilane (RTES) (0.07 mol). The colloidal solutions was immediately characterized and used to prepare the polyelectrolyte-silica films.

Preparation of polyelectrolyte-surfactant complex

The polymer-surfactant complexes were obtained by adding a PAC_nNa solution into a C_xTAB micellar solution under continuous stirring. The complexes are noted as $PAC_nNa\text{-}C_xTAB$. They are formed by electrostatic interaction between the negatively charged PAC_nNa and the positively charged C_xTAB. The preparation method was presented in our previously paper.[25]

Film preparation

Solutions of hydophobically modified polyacrylate (PAC_nNa, n = 18, 10^{-2}M) containing 0.01 M NaCl, PDADMAC (10^{-2} M) and PEI ($5x10^{-2}$ M) were prepared for films deposition. The multilayers were deposited on glass with PEI as substrate, in an alternate way by using PDADMAC and PAC_nNa solutions. The LBL depositions were conducted by a programmable dipping machine (Dipping Robot DR-3, Riegler & Kirstein GmbH). The dipping procedure was reported in a previous study.[25]

To observe the effect of silica nanoparticles on wettability polyelectrolyte-silica films were prepared by layer-by-layer method. In the first step the hydrophobically modified poly(acrylate) films were immersed in silica solution. Then, the films were dried and immersed in a PDADMAC solution. The films obtained were dried and kept in snap-cap vials, in the dark, at room temperature (23◦± 1◦C) and relative humidity of 38 ± 1%.

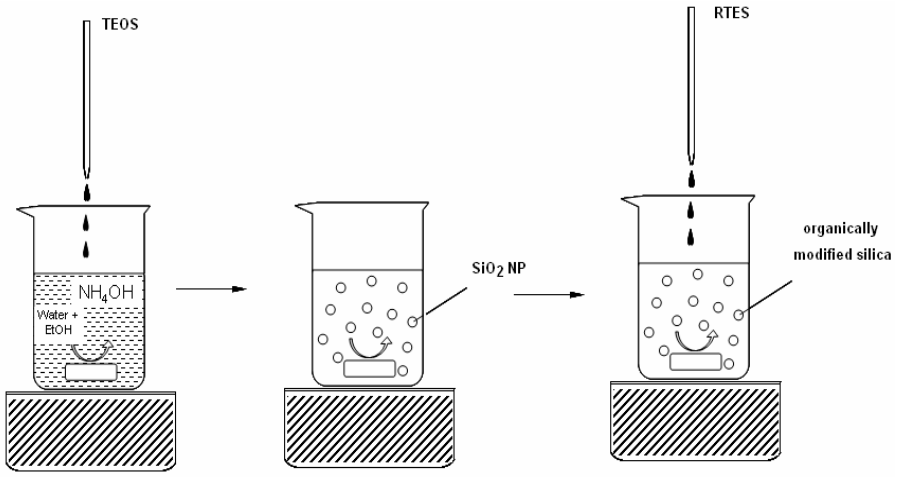

Fig. 6 – Preparation scheme of hybrid silica.

Characterization method

The contact angle measurements were collected using a Drop Shape Analysis System, model DSA1 (FM40 Easy Drop) from KRÜSS GmbH. The water drop volume was of 3 μL, the measurements were done in static regime, at room temperature, in air. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) measurements were performed as previously described.[25] Particle size distribution was measured through Dynamic Light Scattering technique, with a Zetasizer Nano ZS (Malvern Instruments Ltd.). The Fourier transform infrared (FT-IT) spectra were recorded on a Nicolet i-S10 FT-IR spectrometer, Thermo Scientific, using the ATR (attenuated total reflection) device, equipped with single bounce diamond crystal, and 32 scans at a resolution of 4 cm^{-1} were recorded in the 400–4000 cm^{-1} spectral region.

CONCLUSIONS

Silica hybrids were prepared by sol-gel method and used to obtain hydrophobic films on glass substrate. The hydrophobically modified poly(acrylate)-surfactant – silica film has a higher contact angle than those without silica nanoparticles. Moreover, the films prepared with SiONp-VTES are less wetable than those with SiONp-MTES. The results of this research are applicable in automobile windows, rearview mirrors, and as antireflexive surfaces.

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