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ORIGINAL PAPER

Hydrophilic–oleophobic behaviour in thin films from fluoromodified nanoclays and polystyrene

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Abstract New nanocomposite thin films were prepared by spin coating technique from polystyrene (PS) and montmorillonite (MMT) modified with perfluoropolyether cationic ammonium salts (FOMMT). The coating thickness was tuned by changing the solution concentration, and it was measured by the scratching method with atomic force microscopy (AFM). Demodulation AFM images of the higher thickness (>100 nm) PS/FOMMT nanocomposite coating do not show any phase difference suggesting the formation of a homogeneous structure, while the corresponding demodulation image of the lower thickness (ca. 60 nm) PS/FOMMT nanocomposite film revealed the presence of two different phases, which may be attributed to fluoromodified clays and polystyrene. Surface characterization was made through contact angle (CA) measurements and it showed unexpectedly low surface tension dispersive component γ_s^d (around 12 mN/m) and a very high polar components γ_s^d (50 mN/m) in the case of the lower thickness PS/FOMMT nanocomposite coating.

Keywords Fluorinated clay · Oleophobic · Hydrophilic · Nanocomposite · AFM

Introduction

The development of easy cleaning or possibly self-cleaning surfaces is one of the main issue of modern nanotechnology, and examples span from photoinduced superhydrophilic TiO_2 films [1, 2] to biomimetic surfaces such as those inspiring to plant leaves [3] and the wings of insects [4].

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On the other hand the use of fluorinated polymers or oligomers to impart water and oil repellency to many substrates (textiles, paper, stones) is a well established technology [5] and it has been largely exploited during the last 3–4 decades. Surfaces coated with fluoropolymers become non-wettable by both water and most low surface tension liquids, and therefore are strictly stain-resistant. However once stained, the following cleaning step can be difficult because of the too high contact angle (CA) between water and such a surface. In many cases the obtainment of an oleophobic but at the same time hydrophilic enough surface would be preferred, even if much more difficult to achieve.

The design of hydrophilic–oleophobic surfaces is often based on the realization of stimuli-responsive materials combining moieties of largely different surface tension, and some examples are reported in the recent literature. For example effective glass surface treatments able to change the wettability behaviour when put in contact with different surface tension fluids (flip–flop behaviour) were described starting from fluoroalkylated oligomeric silanes containing hydrophilic monomers [6]. Segmented polyurethanes containing an assembly of polyoxyethylene, polydimethylsiloxane, and perfluoropolyether as soft blocks can switch into oleophobic, hydrophobic or hydrophilic surface behaviour [7] in response of the changing polarity of the contact liquid. Stimuli responsive surfaces were produced also by complexation of cationic fluorinated surfactants [8] on negatively charged plasma treated polymer surfaces, while more recently non-ionic fluoroalkylic surfactants were covalently immobilized on silane-treated glass to obtain self-cleaning antifog coatings [9, 10].

In the other hand, polymer based nanocomposites containing organophilic clays have become a quite popular class of advanced materials [11, 12] showing relevant improvements especially as far as mechanical, barrier and chemical (for example reaction to fire) properties are concerned. Relatively little information is however available about designing clay-based nanocomposite materials with tailored surface properties. Accordingly, in this communication the peculiar wettability behaviour of new polymer nanocomposite thin films solution blended from fluoromodified clays (FOMMT) and polystyrene is presented. The clays were prepared by cation exchange process of sodium montmorillonite with perfluoropolyether quaternary ammonium salts [13]. It was found that an interesting hydrophilic–oleophobic behaviour can be obtained by controlled deposition of nanometric films, opening the way to the development of novel easy-cleaning surface coatings for many possible applications.

Experimental part

Materials

A polystyrene sample (Aldrich) with $M_n = 217{,}000$ and $M_w/M_n = 1.49$ was used for the experiments. Molecular weight distribution was measured by Gel Permeation Chromatography (GPC) using a Waters 510 instrument, equipped with a refractive index detector (Waters 410 differential refractometer) and a set of 4 Waters Styragel

HR columns packed with crosslinked styrene–divinylbenzene copolymer particles (porosity 10^2–10^5 Å). Tetrahydrofuran (THF) was used as eluent at 30 °C and GPC chromatograms were calibrated with standard polystyrene samples.

The clay used in the formulation of the nanocomposite thin films was a fluoro-modified montmorillonite (FOMMT) whose preparation was previously described [13]. It consisted of a sodium montmorillonite clay functionalized by cation exchange with a perfluoropolyether quaternary ammonium salt, having the following chemical formula:

$$\mathrm{Cl(CF(CF_3)CF_2O)_3CF_2CONHCH_2CH_2N(CH_3)_3^+I^-}$$

The extent of fluoromodification in FOMMT clay is about 61% w/w as resulted by thermogravimetric analysis.

Chloroform (from Aldrich) was used as solvent as received.

Sample preparation and characterization

The PS sample was dissolved in chloroform at two different concentrations (0.6 and 1.0% w/v), and then the FOMMT clay (3 phr) was added. The mixture was then kept under magnetic stirring for 30 min. Thin films were successively prepared by spin coating the PS-FOMMT solutions on a glass microscope slide at 1,600 rpm for about two minutes at ambient temperature, using a Laurell WS-400Bz-6NPP single wafer Spin Processor.

Atomic force microscopy (AFM) topographic and demodulation images were obtained with a NSCRIPTOR™ DPNWriter™ (Nanoink, USA) instrument in tapping mode equipped with standard silicon tips (nominal resonant frequency 320 kHz) at ambient pressure, temperature and humidity. The mean spring constant of these tips was 0.2 N/m. The mean surface roughness (R_a), which is the average deviation of the surface heights relative to average mean of these peaks in a scanned image, and the root–mean–square roughness (R_{rms}), which is the standard deviation of measured data on the analyzed surface, were calculated according to the following equations:

$$R_a = \sum_{n=1}^{N} \frac{|z_n - \bar{z}|}{N} \tag{1}$$

$$R_{rms} = \frac{\sum_{n=1}^{N} (z_n - \bar{z})^2}{N} \tag{2}$$

where $\bar{z}$ is the average mean of measurements heights and N is the number of points included in the analyzed surface. Thickness of the nanocomposite layer was also evaluated by AFM-tip scratch test [14–16] in contact mode. Scratches were performed on the polymer films by scanning the tip repeatedly back and forth over a square area (10 × 10 μm^2), while the normal force applied was set to a value high enough to penetrate the layer but low enough to avoid significant damage or scratch of the surface. After scratching, the area was imaged orthogonally to the scratch direction in the non-contact mode using the same tip used for scratching. This procedure was needed in order to retrieve the observed area after tip replacement.

Finally, the scratch depth, i.e. the polymer layer thickness, was evaluated by image analysis. For each scratch, at least three cross-sections normal to the scratch direction were randomly chosen for statistical analysis of scratch profiles.

Contact angle (CA) measurements were carried out with an OCA20 instrument (Dataphysics Co.), equipped with a CCD camera and with a 500 μl-Hamilton syringe to dispense liquid droplets. Measurements were made at room temperature by means of the sessile drop technique. At least ten measurements were performed at different places on each sample and results were averaged. Bidistilled water, the highest purity grade of diiodomethane and *n*-hexadecane (n-C_{16}) were used as probe liquids, and the delivered volume was 3 μl. CA measurements were carried out with time interval of 1 s between drop deposition and the measurement. The water and diiodomethane CA measurements were used to determine the surface tension of the coatings. Total surface tension γ_s, and their dispersive γ_s^d and polar γ_s^p components were calculated by means of the geometric mean theory of Owens, Wendt, Rabel and Kaelble [17, 18] (OWRK method), using for water $\gamma_l = 72.3 = \gamma_l^d + \gamma_l^p = 18.7 + 53.6$ mN/m, and for diiodomethane $\gamma_l = 50.8 = \gamma_l^d + \gamma_l^p = 49.5 + 1.3$ mN/m.

Results and discussion

Polystyrene was chosen as base polymer since it is a quite hydrophobic but very oleophilic material, and therefore possible surface wettability changes induced by the presence of fluorinated nanoclays could be easily detected.

Figure 1a shows, as example, the AFM topographic image of the scratch made on the PS/FOMMT film cast from 1% w/w solution, while Fig. 1b shows the corresponding line profile and thickness determination using AFM-tip scratch test. The relevant pile-up in Fig. 1 is due to polymer displaced during scratching. For a better accuracy in thickness measurements, the average depth of each scratch was successively measured in tapping mode. Measured film thicknesses for 1.0 and 0.6% nanocomposite films are reported in Table 1 as the result of at least three independent scratches. It is obvious that solution concentration is a major factor controlling the thickness of the film applied by spin coating.

Surface composition and structure of the coatings were studied by AFM in tapping mode. The demodulation imaging of the higher thickness (144 ± 7 nm) PS-FOMMT nanocomposite suggests the formation of a homogeneous surface material and the coating does not show any phase difference (Fig. 2a). On the other hand the demodulation image of the lower thickness (61 ± 2 nm) PS-FOMMT nanocomposite film (Fig. 2b) shows the well defined presence of two different phases or materials, which could be tentatively attributed to the fluoromodified clay and PS. As a matter of fact, while no significant differences in roughness between neat PS and 144 nm thick film was observed as reported in Table 1, a some rougher surface was measured in the case of 61 nm thick film, due to the presence of clay outcrops on the surface. Moreover Fig. 1a shows that the clay particles are uniformly distributed in the matrix, although the dimension of the particles is not the same and sometimes they tend to aggregate in larger structures. When sufficiently well dispersed, most

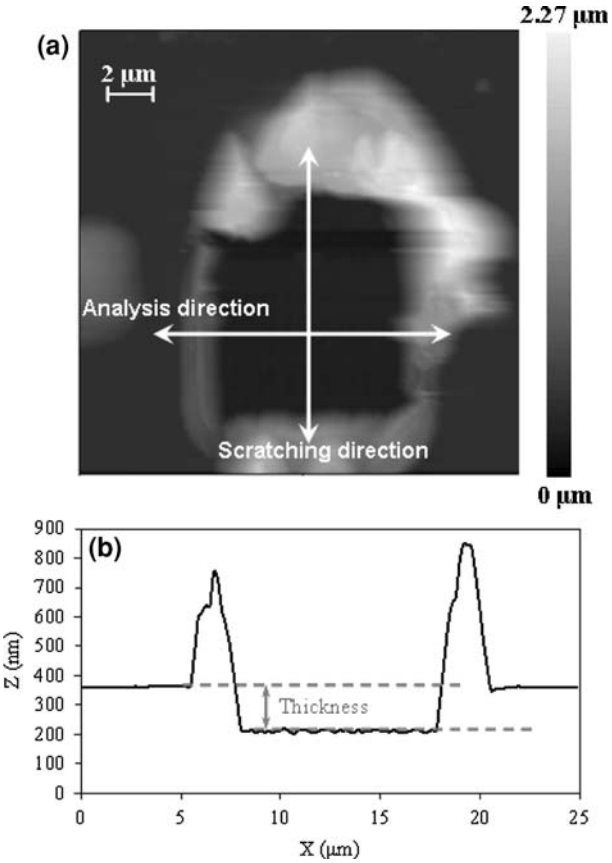

Fig. 1 **a** AFM topographic image of the scratch made on the PS/FOMMT film cast from 1% w/w solution and **b** its corresponding line profile and thickness determination according to the AFM-tip scratch test

Table 1 Coating thickness and surface roughness for the different nanocomposite films containing 3 phr of FOMMT

Sample	Casting solution (% w/w)	Thickness (nm)	R_a (nm)	R_{rms} (nm)
PS	1.00	ND	0.33	0.46
PS/FOMMT 0.6%	0.58	61 ± 2	0.89	1.42
PS/FOMMT 1%	1.00	144 ± 7	0.34	0.67

clay structures show lateral thickness around 30–50 nm as shown in Fig. 3, and therefore at mostly intercalated nanostructures are likely to be formed.

Surface tension of nanocomposite coatings was estimated through static CA measurements. Experimental values and calculated surface tension components according to the OWRK method are reported in Table 2. It can be observed that while total surface tension and its components remain substantially the same for the

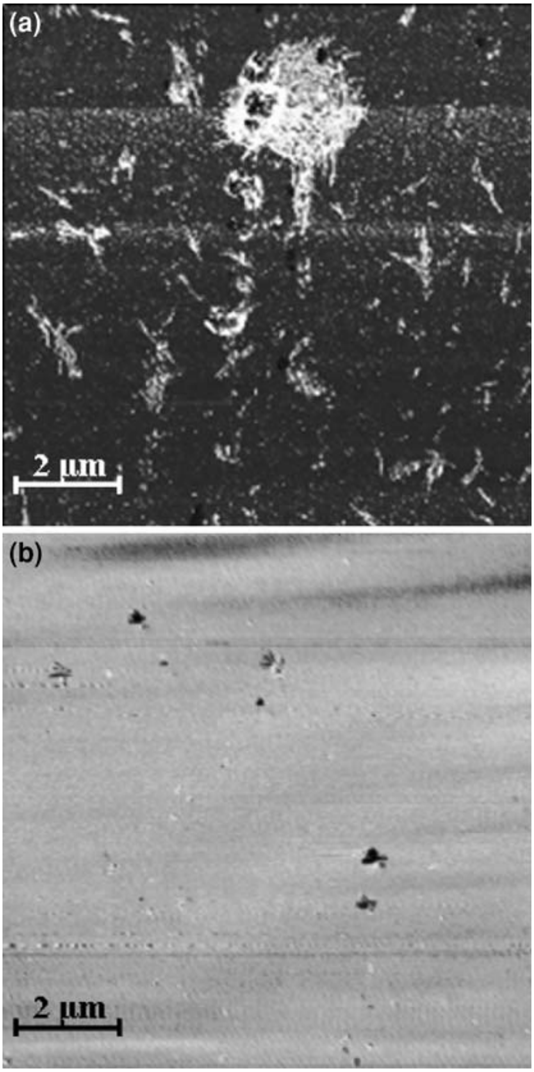

Fig. 2 Tapping mode AFM demodulation images of PS/FOMMT coating from **a** 0.6% solution and **b** 1% solution

144 thick film and neat PS, they show a dramatic change for the thinner coating. In such a case the polar component γ_s^p passes from 2.0 to 49.9 mN/m whereas the dispersive component sharply decreases from 38.0 to 12.1 mN/m. At the same time the CA against *n*-hexadecane is high enough to impart some practical oleophobicity to the nanostructured polystyrenic surface, which otherwise easily absorbs hydrocarbon droplets. Images reported in Fig. 4 show the different shape of water and hexadecane droplets put on contact with the 0.6% PS/FOMMT nanocomposite. It is worth to underline that such result was achieved with an overall very limited amount of fluorinated surfactant within the material (about 1.6% w/w).

Also in case of PS/FOMMT nanocomposite films applied from higher concentration solution (i.e. thicker coatings) no significant differences were

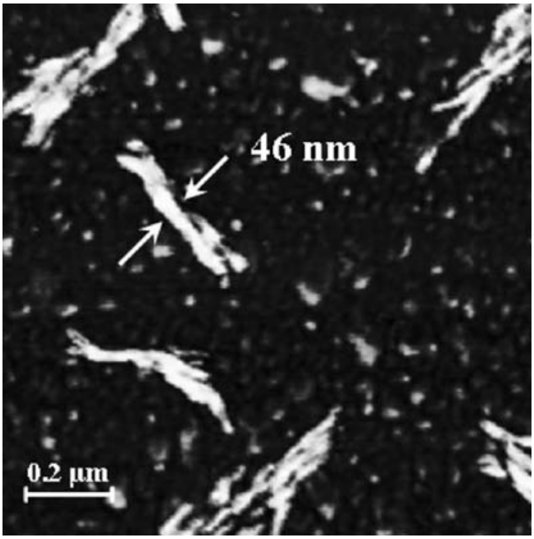

Fig. 3 Higher magnification tapping mode AFM demodulation images of PS/FOMMT surface spin coated from 0.6% solution

Table 2 Static contact angles, total surface tension and its components for neat PS and PS/n3-FOMMT nanocomposite coatings

Sample	Casting solution (% w/w)	Contact angle ± SD (°)[a]			Surface tension γ_s (mN/m)		
		H_2O	CH_2I_2	n-C_{16}	Total	Dispersive component γ_s^d	Polar component γ_s^p
PS	–	91 ± 1	35 ± 1	–[b]	42.1	40.9	1.2
PS/FOMMT 0.6%	0.60	32 ± 4	74 ± 2	58 ± 5	62.0	12.1	49.9
PS/FOMMT 1%	1.00	89 ± 1	40 ± 2	15 ± 1	40.0	38.0	2.0

[a] Errors are shown with the standard deviation (SD)

[b] Immeasurably low

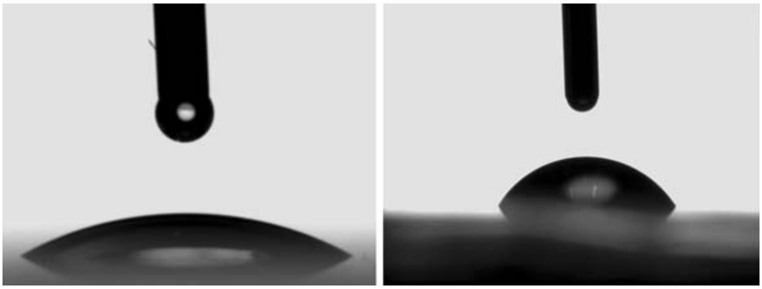

Fig. 4 Shape of liquid droplets put in contact with the PS/FOMMT spin coated from 0.6% solution surface: water (*left*) and *n*-hexadecane (*right*)

observed with the wettability behaviour of neat PS, and therefore it seems to exist a critical concentration or film thickness to show a practical oleophobic behaviour; this thickness is likely to be dependent on the degree of delamination of FOMMT particles within the polymer matrix.

These data seem to be consistent with the intrinsic surface behaviour of FOMMT clays, previously described in a work of us [13]. Actually CA measurements carried out on pressed clay discs showed the presence of evident kinetic effects with a progressive time dependant increase of wettability and hydrophilicity as typical of stimuli-responsive multiphasic surfaces. In case of PS/FOMMT thin films the determination of hysteresis through advancing and receding CAs measurements against water was not feasible since after the first wetting cycle the following CA was to small to be reliably determined by sessile drop technique.

The apparently anomalous CA values measured could be tentatively related also to the formation of a rough mixed surface structure according to the classical Cassie and Baxter [19] model:

$$\cos\theta_{cb} = \Phi_s\left(\cos\theta_y + 1\right) - 1 \tag{3}$$

where θ_{cb} is the apparent CA measured on the rough Cassie–Baxter surface, θ_y is the static CA on the corresponding flat surface, and Φ_s is the fraction of solid outcrops wet by the liquid. By using $\theta_y = 45.2°$ as CA against water of the pure fluoromodified clay [13], it would result a Φ_s value as high as 0.92, which seems however too high according to AFM direct observations.

Conclusive remarks

A series of polystyrene/fluoromodified montmorillonites nanocomposite thin films were prepared by solution blending and spin coating technique. It has been shown that the formation of fluorinated clay outcrops is promoted by a controlled deposition of a very thin coating film. While keeping an overall small surface roughness, in this case a dramatic change in the wettability behaviour occurs with the formation of hydrophilic–oleophobic effects. The surface markedly increases the polar component of the surface tension while the dispersive component decreases.

AFM morphological analysis suggests that only a very partial delamination of clay platelets occurs, and therefore a further optimization of nanocomposite composition and formulation may lead to the development of very effective hydrophilic–oleophobic nanocomposite materials. Applicability of the Cassie–Baxter model to the nanocomposite materials of the present work should be checked on a wider range of samples and experimental conditions.

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