



Hierarchical dual-sized film surface morphologies self-generated from fluorinated binary latex blends boost hydrophobicity and lipophobicity

Chengcheng Yang^{a,b}, Valter Castelvetro^{b,c,*}, Sabrina Bianchi^b, Michele Alderighi^b, Yongming Zhang^a

^a School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, 200240 Shanghai, PR China

^b Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy

^c Istituto per i Processi Chimico-Fisici, Consiglio Nazionale delle Ricerche (IPCF-CNR), Area della Ricerca, Via G. Moruzzi 1, 56124 Pisa, Italy

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ABSTRACT

Latex films with controlled dual-level nanorough surfaces were obtained by casting from binary blends of fluorinated copolymer particles with a nanostructured core-shell morphology, narrow size dispersity and large size ratios. For this purpose, particles with different size, a common unfluorinated acrylic core copolymer of the self-crosslinking trimethoxysilylpropyl methacrylate (TSPMA) and a hard shell copolymer of either 2,2,2-trifluoroethyl methacrylate (TFEMA) or 1H,1H,2H,2H-heptadecafluorodecyl methacrylate (FMA) were synthesized by multistage emulsion polymerization. The FMA-based particles showed patchy morphologies dictated by the type of β -cyclodextrin used as FMA phase carrier in their synthesis. Four series of binary blends of either TFEMA or FMA copolymer particles with large (3–4 diameters) size ratios were cast into latex films with controlled hydrophobicity and lipophobicity. AFM and electron microscopy results indicate that addition of the small particles disrupts the hexagonal compact packed 3D organization of the large particles, resulting in dual-level nanorough surfaces and high water contact angles (up to $\theta_w = 127^\circ$ in the as cast films, and $\theta_w = 135^\circ$ upon aging or thermal annealing causing surface restructuring and TSPMA sol-gel condensation) with respect to the parent single component films. The proposed approach provides a straightforward route for the fabrication of robust coatings and films with tunable lipophobic and highly hydrophobic surfaces.

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1. Introduction

Fluorinated polymers are generally characterized by high chemical and thermal stability as well as low refractive index, dielectric constant and surface energy [1–5]. While these are among the main requirements for coating applications, the poor adhesive, cohesive and mechanical properties of most highly fluorinated polymers, their insolubility in common unfluorinated solvents and high cost prevent their widespread application. The above limitations can be partly overcome by copolymerization of fluorinated and unfluorinated monomers [6] and by formulating the coating polymer as a water borne (WB) film-forming dispersion, or latex. In particular, fluorinated acrylic copolymers are common components of highly water- and oil-repellent WB coatings [7,8]; among them, those containing monomers with long ($C > 6$) perfluoroalkyl side chains ensure the best performances, with surface energies as low as 8 mN/m [9–11].

Formulation of coating materials based on WB fluorinated polymers poses several problems, but it also offers new opportunities

* Corresponding author at: Dipartimento di Chimica e Chimica Industriale, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy. Fax: +39 050 221 9256.

E-mail address: vetro@dcci.unipi.it (V. Castelvetro).

with respect to the less environmentally friendly solvent-based systems. Among the problems, a most relevant one for coating applications is the poor cohesivity and adhesivity typical of highly fluorinated polymers, which adds up to the issue of achieving a good cohesivity and water resistance common to all films and coatings obtained from aqueous polymer dispersions. Three main strategies have been proposed to tackle this latter issue, while minimizing the emission of solvents typically added as film-forming aids: (i) introduction of reactive comonomers for delayed crosslinking of soft, film-forming particles [12–14]; (ii) using nanostructured latex particles in which a hard core is coated by a soft film-forming shell, or even with the reverse morphology [15,16] (in the latter case the film-forming ability may be preserved if the hard shell is not uniform, as in patchy core-shell particles) [17,18]; (iii) blending soft (deformable) and hard (nondeformable) particles, where soft and hard are referred to polymers with T_g well below and well above ambient temperature, respectively, to preserve film-forming behavior [19]. While the above strategies may find general application, the latter two approaches are of specific interest for fluorinated coatings as they may allow a significant reduction of the fraction of costly fluorinated polymer without affecting the film surface properties. In addition, they provide a route for obtaining well-defined nanostructured morphologies,

which can be of interest in the design of high performance coatings and films.

Latex films based on core-shell particles with shell composition spanning from the slightly fluorinated copolymers of 2,2,2-trifluoroethyl methacrylate (TFEMA) [20,21] to the highly fluorinated ones based on 3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorodecyl methacrylate (FMA) have been investigated, although in the latter case, complex formulations [22–26] or poorly controlled particle morphologies [27–29] caused by the negligible solubility of FMA in most aqueous surfactant solutions resulted in not optimized latex film properties. Recently, an efficient route for the synthesis of film-forming nanostructured latex particles with a soft unfluorinated BMT core (a copolymer of butyl acrylate, methyl methacrylate and the sol-gel reactive trimetoxysilylpropyl methacrylate, TSPMA) and a hard but “patchy” FMA copolymer shell has been described, in which controlled growth of the shell layer is achieved by semi-continuous starved feed emulsion polymerization mediated by three different β -cyclodextrins [18].

On the other hand, binary blends of hard and soft latex particles may not only improve film formation and performance, but also allow the fabrication of nanorough super-hydrophobic surfaces. In fact, super-hydrophobicity is typically achieved through a combination of suitable chemical composition for low surface energy, and of multiscale hierarchical micro- and/or nanoroughness for synergistic amplification of the intrinsic material properties [30–33]. Examples of such super-hydrophobic nanorough surfaces based on binary blends of particles with narrow distributions of two largely different sizes have been described, in which one of the components can even be a hydrophilic and not film-forming inorganic colloid [34,35]. Generation of controlled surface roughness at the nanometer scale by such bimodal colloidal dispersions involves some kind of hierarchical self-assembly of the particles, which may be governed not only by the particle size ratio and particle surface composition, but also by the combined effect of Brownian motion, convective flows and capillary forces acting during the initial stage of water evaporation, when the single particles are still flowing [36,37]. In any case, for practical coating applications more robust film-forming materials are needed. These can be based on a combination of the above concepts of binary latex blends and fluorinated core-shell particles for atom efficiency and property optimization [38].

Keddie and coworkers studied in detail the surface and bulk morphology of unfluorinated latex films and, among others, of those based on either soft-soft (large-soft and small-soft) or large-soft and small-hard binary particle blends [39,40]. With a 6:1 particle size ratio, by increasing the fraction of small particles, they observed decreasing void volume concentration along with decreasing surface roughness up to a critical volume fraction $V_c \approx 16\%$ of small particles, as a result of interstitial distribution of the small particles until a continuous phase of small particles surrounding the large ones is obtained. At higher concentrations, the surface morphology and film properties depend on the hard or soft nature of the small particles: small-hard particles cause an increase of surface roughness up to a maximum value $V_m \approx 55\%$ when the film integrity is lost, in analogy with the concept of critical pigment volume concentration (CPVC [15]); on the contrary, small-soft particles are film-forming and their increase above V_c does not induce any further increase of surface roughness.

In the present work, a series of shell-fluorinated copolymer particles with different sizes and compositions have been synthesized and blended to obtain highly hydrophobic latex films. A hydrophobic surface was expected to arise from the combined contribution of the surface energy-lowering fluorinated shell and of the nanoroughness self-generated by appropriate combinations of two types of particles with similar composition and internal structure, but

largely different size. In particular, latex particles with narrow size dispersity and a copolymer of either the slightly fluorinated TFEMA or the highly fluorinated FMA in the shell have been used to prepare binary latex blends with large (3–4 diameters) particle size ratios, which were then cast into films to obtain surfaces with a range of nanostructured morphologies. The reactive comonomer TSPMA was introduced in both core and shell copolymers to lower the interfacial tension, prevent phase inversion between core and shell copolymers and possibly contribute to the film properties [41–44]. In fact, sol-gel condensation of its alkoxy silane group may not only result in delayed crosslinking of the latex films but also in the stabilization of the fluorinated film surface against dynamic restructuring. The interfacial properties and morphology of the films prepared both from the binary latex blends and from the parent single component latexes were investigated by static and dynamic contact angle measurements and scanning probe microscopies. Contact angle data were also collected after thermal annealing to evaluate the morphological and chemical transformations resulting in surface restructuring through segmental migration and conformational dynamics of the fluorinated polymer (particularly the FMA copolymer) and through chemical crosslinking by sol-gel condensation of the alkoxy silane groups.

2. Experimental section

2.1. Materials

Butyl acrylate (BA) and 3-trimethoxysilylpropyl methacrylate (TSPMA, Aldrich) were distilled under vacuum and stored under nitrogen at -20°C . Methyl methacrylate (MMA, Aldrich) and 2,2,2-trifluoroethyl methacrylate (TFEMA, Apollo Scientific Ltd) were distilled under nitrogen and stored at -20°C . 3,3,4,4,5,5,6,6,7,7,8,8,8-Heptadecafluorodecyl methacrylate (FMA, Fluorochem) was purified by passing its acetone solution through an inhibitor remover column (Aldrich) followed by removal of the solvent at reduced pressure. Potassium persulfate (KPS, Sigma-Aldrich), sodium dodecyl sulfate (SDS, Aldrich), β -cyclodextrin hydrate (CD, Aldrich), randomly methylated β -cyclodextrin (MeCD, Cavasol[®]W7 M, Wacker; 1.6–1.9 substituted hydroxyls per glucopyranose unit; water solubility at $25^\circ\text{C} \sim 800\text{ g/L}$), hydroxypropyl β -cyclodextrin (HpCD, Cavasol[®]W7HP, Wacker; 0.6–0.9 substituted hydroxyls per glucopyranose unit; water solubility at $25^\circ\text{C} \sim 2300\text{ g/L}$), Brij[™]58P (oligoethoxylated cetyl alcohol with 20 ethyleneoxide units, HLB = 15.7, Fluka), hexadecane (Aldrich, >99%) and the buffering salts sodium hydrogen carbonate (NaHCO_3 , J.T. Baker) and sodium dihydrogenphosphate (NaH_2PO_4 , Aldrich) were used as received. HPLC-grade water was used for the polymerizations.

2.2. Characterization methods

The monomer conversion and the solid content of the final latex were determined using a Mettler Halogen HB43 Moisture Analyzer by heating up to constant weight a given amount of latex (W_L) in the presence of inhibitor (hydroquinone, Aldrich). The obtained conversions (nominal, that is, assuming as totally converted the nonvolatile FMA) were typically in the 90–95% range. Photon Correlation Spectroscopy (PCS) was used to measure intensity-weighted z-average particle diameters, d_p , by means of a Brookhaven 90 Plus Dynamic Laser Light Scattering (DLLS) instrument equipped with a 35 mW laser and an Avalanche photodiode detector, collecting the scattered light at 90° . Particle size, particle size distribution and polydispersity (PD) were calculated from the decay constant obtained by a second-order fit of the Cumulant analysis of the autocorrelation function, using CONTIN and NNLS (Non Negative Least Square) data elaboration. Differential scanning

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