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Morphology and Microchemistry of Colloidal Polymers

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Summary: Colloidal polymers are highly versatile due to the variety of properties and functions that can be created by changing monomer composition, surfactant, initiator and reaction protocol. Microchemical and morphological observation of the particles and particle aggregates as well as films and monoliths made with them is allowing us to understand the connections between nanosized structural features and macroscopic properties and this is essential for the creation of valuable new polymer materials. Electron spectroscopy imaging (ESI) in the transmission electron microscope (TEM) uses electron energy loss spectroscopy (EELS) to provide a wealth of information on particle constituents and their topological distribution, allowing a number of correlations with the polymer mechanical, thermal, optical and electrical properties. On the other hand, scanning probe microscopy (SPM) techniques allow direct measurement of particle and film properties such as adhesion, stiffness, electrostatic potential as well as rheology information with high spatial resolution, down to 10-20 nm and under many different experimental conditions. Information from the joint use of these techniques is revealing a wealth of nanostructures within colloidal polymers requiring a revision of many preconceived ideas on these materials.

Keywords: colloidal polymer; electron microscopy; latex; microchemistry; morphology; scanning probe microscopy

Introduction

Materials electron microanalysis is largely done using the scanning electron microscope (SEM) or the scanning transmission (STEM) instruments associated to x-ray spectroscopy (EDX), but these techniques suffer from two major limitations: in SEM, spatial resolution is usually lower than in the transmission microscopes and the spectral sensitivity of EDX is too low for the light elements that are usually found in polymers. For these reasons, the use of analytical electron microscopy has been largely restricted to inorganic solids (metals, semiconductors, ceramics).[1]

This situation was changed during the past two decades thanks to the introduction of electron spectroscopy imaging in the transmission electron microscope (ESI-TEM), that allows the observation of the distribution of light elements (e.g. C, F, O, S, Na) in a sample, with a high spatial resolution.[2,3]

A significant difficulty in the use of TEM is that thick samples produce low contrast in the predominant bright-field imaging mode. The observation of contrast within samples requires the use of thin sections and in the case of polymers these are often prepared by cryo-ultramicrotoming. what is a significant difficulty: often, sample preparation takes much longer and the outcome may be much less predictable than the actual microscopy examination.

However, in the case of polymer colloids[4] it is often possible to examine

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samples following minimum preparation, especially if the samples are made out of nanoparticles with diameters below 100 nm. On the other hand, low-T_g particles that are spontaneously flattened over the carbon film supports used in the microscope often become sufficiently thin to be examined without any further preparation. Larger particles can also be directly observed but micro-chemical information can only be acquired from the areas adjacent to the particle surface, due to multiple electron scattering in the thicker areas. On the other hand, it is also possible to acquire images using inelastic scattered electrons using electron energy filters (EFTEM)[5,6] and these allow the observation of morphological features of thicker samples as well as particle aggregates.

Another important development from the past two decades is the introduction of a number of SPM techniques that allow the mapping of many properties on a solid sample, either dry or under a liquid. Among other properties, it is possible to observe and to measure topography, adhesion as well as Young modulus, ability for viscous dissipation, electrostatic potentials,[7,8] magnetic and chemical binding properties with a spatial resolution in the 10–20 nm range. Sample preparation involves relatively few steps but these have to be done carefully to allow useful data interpretation. The use of ambient conditions and the possibility to change pressure and humidity or to observe immersed samples are extremely helpful.

This is a short account on recent work done in the authors' laboratory together with some new results.

Experimental

Experiments done in this laboratory used the following equipment: a Topometrix Discoverer SPM, a Shimadzu SPM and a Zeiss CEM-902 TEM. Sample ultramicrotoming was done in Leica cryo instruments.

The techniques used for latex sample preparation and microscopy examination are described in detail in previous work from this laboratory.[9–12]

The following samples were used:

1) a commercial styrene-acrylic latex used in architectural paint was supplied by Denver company (São Paulo);
2) a low T_g styrene-butyl acrylate-acrylic acid latex was prepared in this laboratory, following a procedure described in previous work but using a nonylphenol ethoxylated surfactant with an average 40 ethylene oxide residues per molecule;[13]
3) natural rubber latex was acquired from a local producer (Riobor) that blends latex collected from different rubber tree plantations in São Paulo state;
4) a clay (Na-Cloisite, from Southern Clays)-natural rubber composite was prepared according to a recent procedure from this laboratory.[14]
5) poly(styrene-co-hydroxiethylmethacrylate) was prepared in this laboratory following ref. 15.

Results

In this laboratory, analytical electron microscopy and scanning probe techniques have been jointly used and they produced a wealth of new interesting information, as follows:

1. The distribution of chemical constituents throughout the particles and within each particle may be rather non-uniform thus accounting for non-uniformity of latex properties and also of films or bulk polymer[11]
2. Non-latex components are also detected, as observed in Fig. 1 that shows a bright-field image together with an energy-filtered image (EFTEM), C and S maps from a commercial styrene-acrylic latex. The comparison of the two elemental maps evidences that a large fraction of the sulfur compounds contained in this

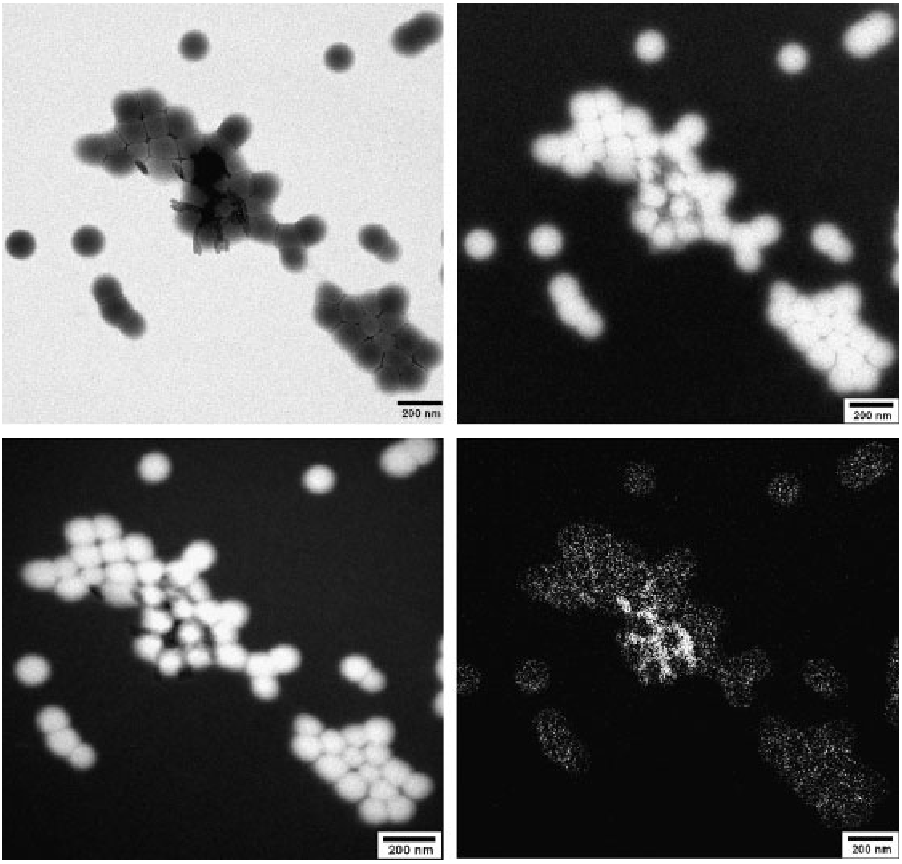

Figure 1.
(top left) Bright-field image, (top right) EFTEM image (25 eV energy loss), (bottom left) C map and (bottom right) S map of a sommercial styrene-acrylic latex used for making paint. The reference bar measures 200 nm.

sample is not found within the particles and thus it is not associated to carbon compounds. This is clear evidence in favor of a mineral S species, perhaps a sulfate salt formed by hydrolysis of sulfate - capped polymer chains. Nevertheless, sulfur is also found at the latex particles, as expected since part of the persulfate initiator residues remains connected to the polymer chains. Moreover, S is not confined to the particle rims, what agrees with existing information on the inaccessibility of part of the sulfate groups by reagents confined to the latex serum as well as with previous information on other latexes.[15] The "dot" aspect of S-rich domains shows that the chain ends are clustered in the particles, evidencing a trend towards micellization within the particles that is easily understood, considering the polar nature of chain ends. These chain-end clusters are in turn hydrophilic sites within the particles imparting them the ability to form occluded water pools, just like in a water-in-oil emulsion.

The observation of mixtures of latex and other particles provides interesting information on the association of different particles. One example is in Fig. 2 that shows an aggregate of latex and aluminum phosphate particles. The phosphate particles appear very dark in the bright-field image as well as in the EFTEM micrograph while the

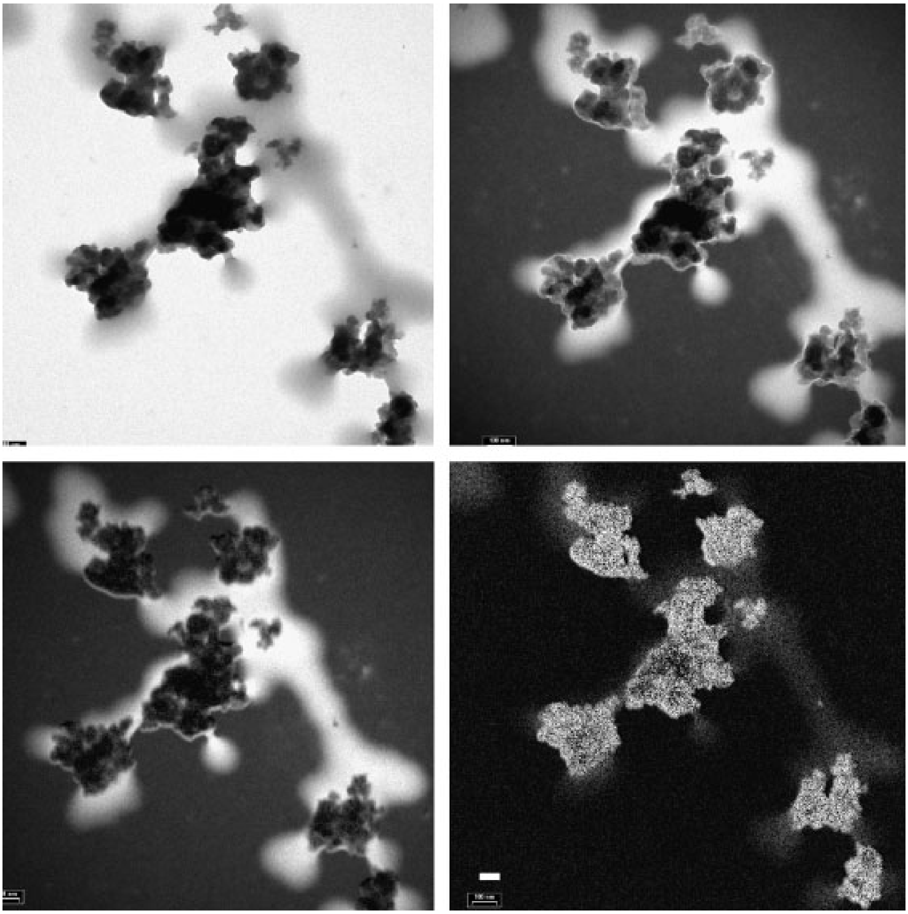

Figure 2.
(top left) Bright-field image, (top right) EFTEM image (25 eV energy loss), (bottom left) C map and (bottom right) P map of a sub-monolayer prepared by drying a dispersion of a styrene-acrylic latex and an aluminum phosphate powder. The reference bar is 100 nm.

coalesced latex particles form a gray film in the bright-field micrograph. The polymer clearly surrounds the aluminum phosphate but a small amount of P is also detected on the polymer domains showing that some phosphate species are absorbed within the polymer.

4) The formation of stable aggregates between clay lamellae and rubber particles, when a dilute dispersion was allowed to dry over the transmission microscope grid was also directly observed (Fig. 3) using different imaging modes that provide different information. For instance, the location of the crystalline clay lamellae is evidenced in the dark-field image where the bright areas coincide with the bright areas in the Si elemental map and also in the EFTEM image. The compatibility of silicate lamellae with polymer is unequivocally demonstrated by the superimposition of many bright domains in the C and Si elemental maps, although there are also areas in which polymer and clay are not superimposed.

The Na map in Fig. 3 also provides an important information: it shows that sodium ions are largely associated to the clay-polymer cluster, where they probably contribute

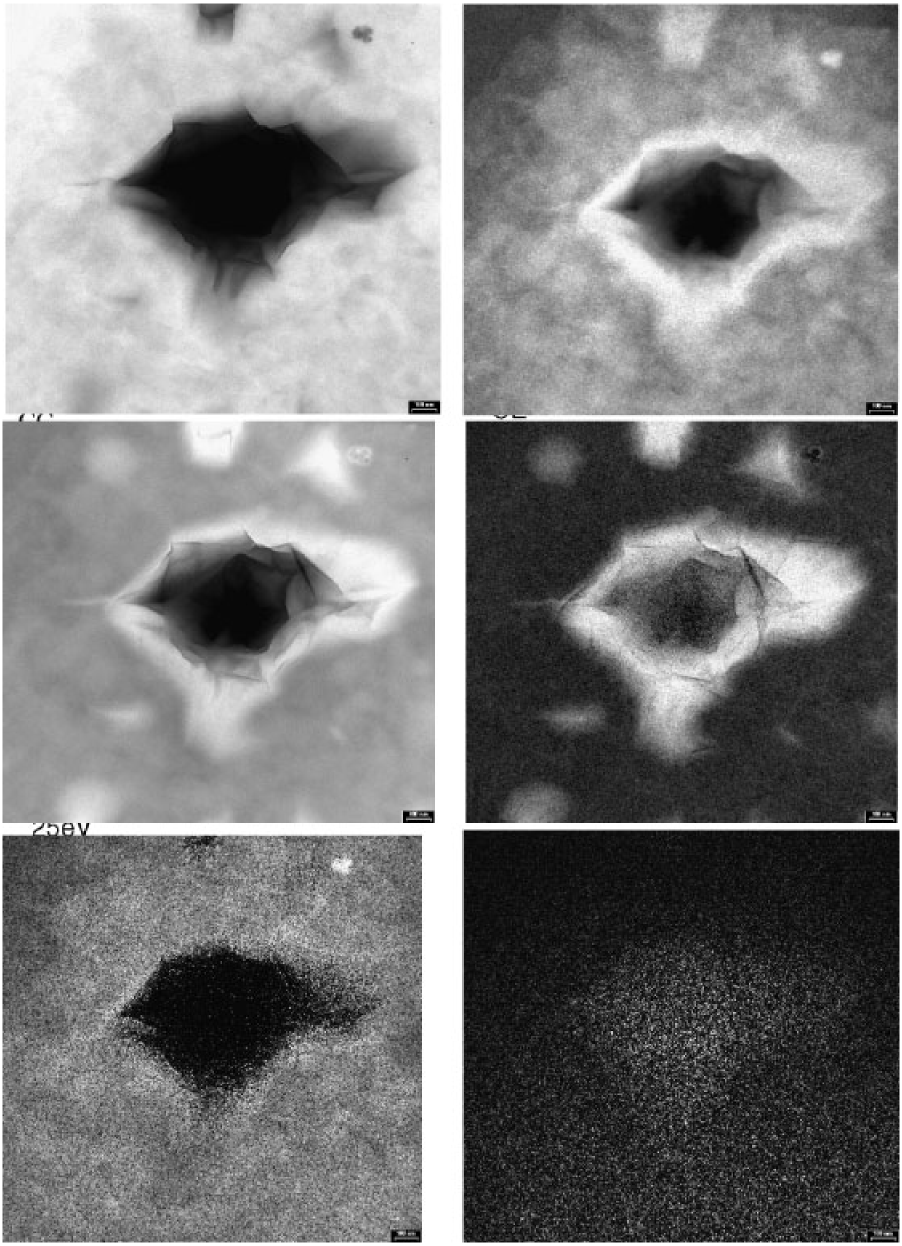

Figure 3.
(top left) Bright-field, (top right) dark-field, (center left) EFTEM image (25 eV energy loss), (center right) C map, (bottom left) Si map and (bottom right) Na map of a sub-monolayer prepared by drying a dispersion of a natural rubber latex and a montmorillonite clay. The reference bar length is 100 nm.

to electrostatic adhesion between the negative clay and polymer particles.

Additional evidence on the adhesion achieved in this case is obtained from the TEM examination of clay-polymer nanocomposite thin cuts where the interfaces between polymer and clay lamellae do not show any voids, as seen in Fig. 4. This is strong evidence in favor of a strong adhesion at the clay-polymer interface that is

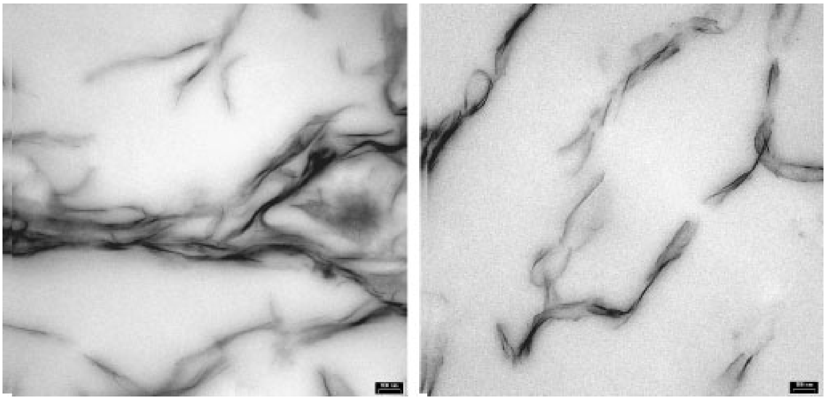

Figure 4.
TEM micrographs of 50-nm thin cuts of a clay-polymer nanocomposite. The clay is montmorillonite and the polymer is a styrene-butyl-acrylate-acrylic acid latex. The scale bar length is 100 nm.

formed by two largely different materials usually considered as incompatible.

Other results that were presented in previous work showed that in some cases, when a heterogeneous latex dispersion dries, domains made out of particle subpopulations are formed, creating large-scale heterogeneities.[16]

Special attention was given to natural rubber, in an attempt to obtain a better understanding of the striking singularities of this polymer, especially considering its mechanical properties. A number of micro-chemical complexities was observed and the most remarkable is the clear association between sites bearing calcium ions and the ability to form gel, showing that these ions have a cross-linking role in the natural rubber.[17–19]

Scanning probe microscopy has also yielded a wealth of information on colloidal polymers and it has a great advantage over electron microscopy that is the possibility to examine colloidal polymers under various environmental conditions. In a previous report from this group, polymer swelling under water was observed, showing that particle swelling is highly anisotropic and providing a visualization of film failure due to swelling pressure.[20]

This raised the question of particle contraction and expansion as a function of relative humidity that can be observed by imaging within an environmental chamber were relative humidity is accurately controlled. An example is given in Fig. 5.

At low humidity the particles display a pronounced curvature that can be inferred from the contrast within particles and from the line-scans that are also shown in Fig. 5. Moreover, particle surface irregularities are more apparent under low humidity. The observed particle flattening is analogous to that observed when particles are immersed in water and it is due to the swelling of the hydrophilic layer of the PS-HEMA particles. These have a core-and-shell structure where the core is predominantly formed by the more hydrophobic styrene residues while the shells are richer in the more hydrophilic ethyl methacrylate residues. For this reason, particle swelling is uneven throughout the particles and it progressively transforms particle shells into softer domains, with increasing humidity. As expected, particle swelling and deformation are reversible (results not shown) as the humidity is alternately raised and lowered.

Discussion

The continuous progress in instrumentation as well as in the methodology and understanding of electron microscopy and scanning probe imaging has been allowing great progress in unraveling the complexities of colloidal polymers and derived materials

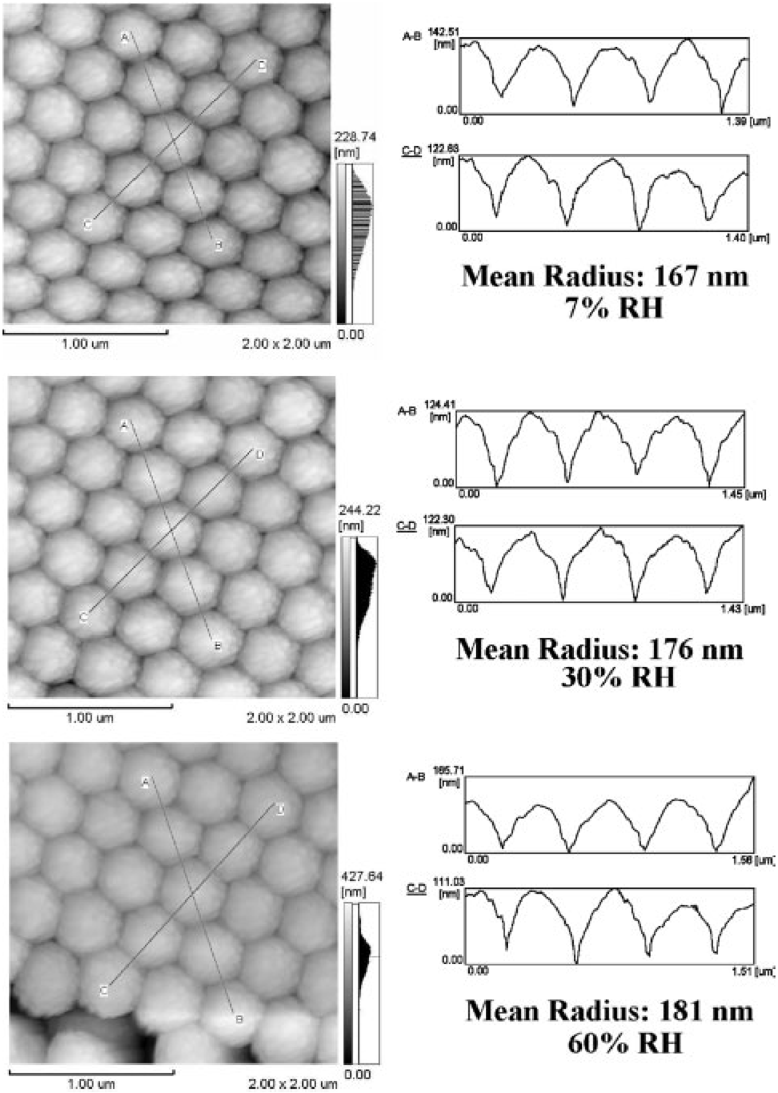

Figure 5.

(left) Non-contact AFM micrographs of PS-HEMA macrocrystal surfaces previously equilibrated with argon at different relative humidities. (right) Line-scans giving height vs. distance across the straight lines drawn in the micrographs.

such as aggregates, nanocomposites and latex blends. As shown in this paper, not only particles themselves are observed but also non-particulate components are detected, producing much new information on how the serum components behave when the latex is dried.

The easy formation of clay-latex clusters upon dispersion drying that is described in this work can be understood following a model based on particle-particle capillary adhesion upon drying, followed by electrostatic adhesion between the two types of negative particles, mediated by counter-ions from the serum.

Existing tools can already answer a large number of questions concerning micro-chemistry and topochemistry of polymer colloids and materials made with them. However, it is often necessary to use different tools and imaging techniques to gather sufficient information, in almost any case. Moreover, the acquisition of the images benefits largely from the information held by the microscope operator, because it is often necessary to decide quickly what has to be done in any specific case, choosing among the ever-enlarging number of imaging modes those that will provide the most relevant information.

In the case of electron microscopy, instruments operating at 50–120 kV already provide a wealth of information and it is hardly necessary to resort to high-resolution microscopes to examine non-crystalline synthetic polymers. Moreover, the larger cross-section of electrons with lower energy is very useful to examine very thin layers formed by non-particulate materials, in the image background.

On the other hand, improvements in the resolution as well as on the imaging speed and scanned area of scanning probe non-contact modes are now highly desired, since current limits leave these techniques in disadvantage as compared to electron microscopy. However, considering that these techniques are still very young, we can expect many significant improvements on these characteristics as well as on new imaging modes.

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