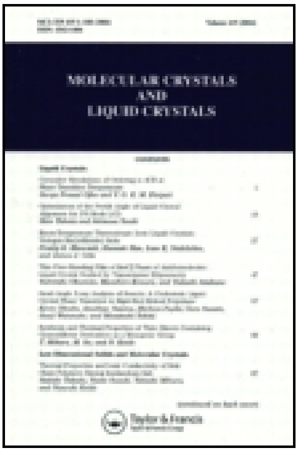

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Particle and Polymer Microchemistry and Electric Domain Mapping

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Particle and Polymer Microchemistry and Electric Domain Mapping

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New microscopy techniques are increasing accessible, yielding hitherto unavailable information on the spatial distribution of chemical constituents in sub-micron and nanosized particles, as well as in polymer films and other materials; this work describes four relevant examples. First, elemental distribution maps of a polystyrene latex obtained by electron spectroscopy coupled to transmission microscopy (ESI-TEM) show that particle C/S ratio is highly variable, evidencing the large differences in polymer Mw's, in different particles. Second, electric potential maps of latex macrocrystals obtained by scanning electron potential microscopy (SEPM) show negative large islands dispersed in a positive continuum, with large electric potential gradients. Backscattered electron imaging (BEI) evidences a core-and-shell structure of silica particles: the particles are made out of smaller domains with variable average atomic number, concentrated at the particle outer layers. The fourth example is a complex columnar structure of electric domains, in crystalline alumina, obtained by SEPM.

Keywords analytical electron microscopy; scanning electron potential microscopy; elemental mapping; domains; particle heterogeneity; backscattered electron imaging.

INTRODUCTION

Colloidal particles are now widely used as precursors of materials, and there is great concern about their sizes and size uniformity, particularly considering the peculiarities of nanoparticle behavior. However, the question of both inter- and intra-particle chemical uniformity [1] has received much less attention, because it requires the use of techniques of recent introduction. There is circumstantial evidence in the literature, showing that some unexpected behaviors could be assigned to particle chemical heterogeneity, and large differences in particle chemical densities were previously observed by using sedimentation in density gradients. However, this question may be more properly addressed by using microscopies endowed with analytical capabilities. In this work we present examples showing results obtained using analytical transmission electron microscopy based on electron energy-loss spectroscopy (ESI-TEM), scanning electric potential microscopy (SEPM) and backscattered imaging in the scanning electron microscope.

METHODOLOGY

Detailed descriptions of the techniques used are given in previous publications from this laboratory. ESI-TEM allows the acquisition of elemental maps of many elements, including the lighter ones except for H.[2] This technique is thus much more convenient than the techniques based on x-ray emission particularly the energy-dispersive methods (EDS), which do not allow the mapping of carbon, oxygen and other important polymer constituents. On the other hand, ESI-TEM imaging is limited to thin samples: either fine particles, particle borders or ultra-microtomy cuts. SEPM is a member of a large family of new techniques within the scanning probe microscopies[3], aiming at the detection of electric features in a sample: local electric potential, electric force and so on. BEI[4] is an older technique with a capability for showing composition chemical heterogeneity in a sample, based on local variations of the average atomic number. It has seldom been used in particle studies due to low-resolution problems, but the availability of field-emission microscopes with resolution capabilities in the nanometer range make this technique highly attractive. Both SEPM and BEI are adequate for the study of thick specimens, films and fracture surfaces, as well as particle sub-monolayers on solid (mica, glass, graphite) substrates. SEPM has the added advantage of not requiring high-vacuum conditions, as the other techniques, and image acquisition is done concurrently with non-contact atomic force (AFM) micrographs. Topography and electric potential maps are then obtained at the same time, for the same sample field.

RESULTS

Inter- and intra-particle latex heterogeneity[5]

The existence of differences in particle chemical composition has been evidenced in many cases, both using copolymer as well as homopolymer latexes, by using analytical transmission electron microscopy associated to energy loss spectroscopy (ESI-TEM). An example is presented in Figure 1, showing a bright-field picture and elemental maps of a polystyrene latex.

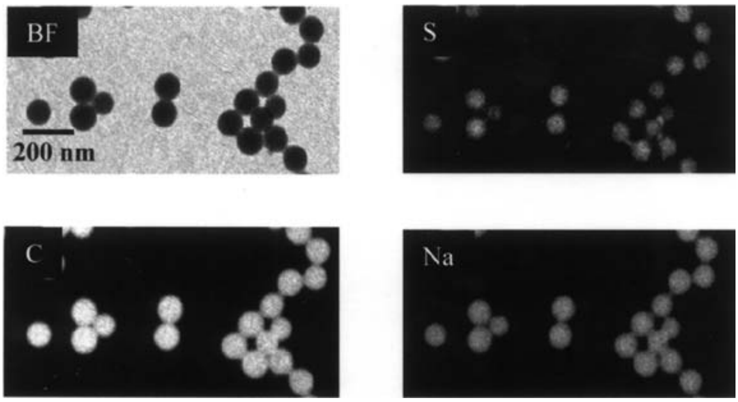

FIGURE 1 Bright-field picture, carbon, sulfur and sodium elemental distribution maps of a polystyrene latex, as observed by ESI-TEM.

The particles are rather uniform in size and carbon distribution is also very uniform, as expected considering that this is the predominating element in the latex polymer. However, sulfur map shows large variations, both within a particle and from one particle to a neighbor. In these particles, sulfur arises from alkylsulfate ion residues from the persulfate initiator. Consequently, particles with a lower sulfur content also should contain polymer with a higher average molecular weigth. The sodium distribution map gives two important informations: first, sodium is found within the particles, thus interspersed with polymer. Second, sodium distribution is more uniform than sulfate distribution, thus suggesting that the particles have significant variation in their net electric charge, since these two species are the predominating ionic charge bearers, in this system.

Ionic domains in latex macrocrystals[6]

Domains with large excess of ions of the same charge are observed in polymer films and other solids fabricated from latex synthesized by emulsion polymerization. These contain ionic charges from the initiator residues, surfactant and counter-ions, which end up trapped in the final product materials. In the case of latex macrocrystals, the location of these charges in otherwise apolar dielectric solids was made by using two different procedures: ESI-TEM and scanning electric potential microscopy (SEPM). A typical result, obtained with poly(styrene-co-hydroxyethylmetacrylate) (PS-HEMA) macrocrystals is shown in Figure 2, displaying the elemental distribution maps of potassium and sulfur obtained by ESI-TEM, together with SEPM electric potential maps.

The elemental maps show that potassium ions concentrate at the particle borders, but these are depleted from sulfur. The electric potential map shows that the particle cores are negative, relative to the particle shells. Consequently, the two types of microscopic information coincide, even though they are completely independent, both considering the actual physics of image acquisition and nature of the entities mapped in each case: elements (potassium and sulfur) or electric charges (positive and negative).

Other work from this laboratory showed that latex macrocrystal defects are often associated with chemically defective particles, showing significant departure from the average chemical composition. Moreover, the fractionation of copolymer latex produces chemically uniform samples, suitable as templates for the making of more complex nanostructures.

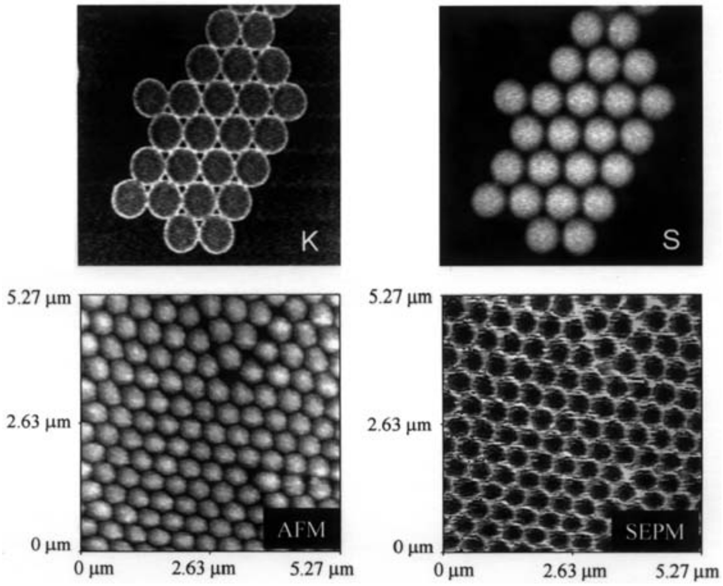

FIGURE 2 K and S elemental maps (top), non-contact AFM and SEPM images of a copolymer latex. Note that the potassium (cations)-rich shell appears positive in the SEPM picture. Z axis ranges AFM: 232 nm ; SEPM: -9.65V to 9.74V.

Core-and-shell structure of silica particles[7][8]

A complex and size-dependent microchemistry for silica particles is evidenced by using another useful approach for the verification of particle heterogeneity, which is back-scattered electron imaging (BEI), in the scanning electron microscope. This technique is widely available but seldom used, and its application to the study of Stöber silica particles shows how powerful is this technique. Figure 3 shows secondary electron (SEI) and BEI pictures from the same field of a colloidal silica. For this non-crystalline sample, BEI contrast is determined by local composition: domains with the higher average atomic numbers are brighter than the others. Comparison of the two images reveal three things: i) the particles appear smaller in BEI than in SEI pictures; ii) there is significant interparticle contrast; iii) there is a brighter background in BEI, particularly at greater distances from the particle aggregate limits.

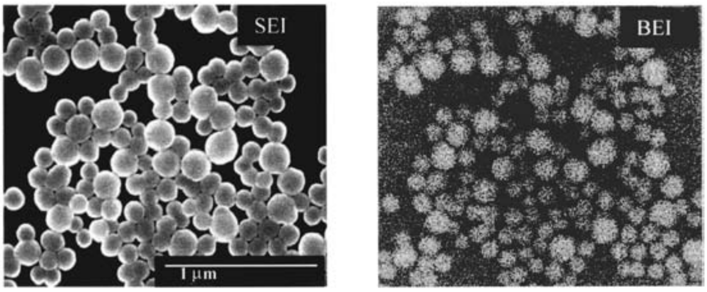

FIGURE 3 Secondary (SEI) and backscattered (BEI) micrographs of silica particles, with effective diameter 141 nm.

All these observations are understood considering that these particles are formed by accretion of poly-silicates formed by hydrolysis of the tetraethoxysilane, and these silicates are non-uniform concerning their degree of hydrolysis and condensation. Moreover, the more hydrous silicates, thus having a higher O/Si ration accumulate at the particle outer layers, making them darker than the inner, less hydrated silica domains.

These results were substantiated by evidence from ESI-TEM and SEPM, and by comparison with another sample of silica prepared by the same procedure, but with a much lower effective particle diameter (36 nm, as compared to 141 nm). The smaller particles do not have a core-and shell structure, but they display strong inter- and intra-particle contrast, in every imaging mode.

Electric domain structure in alumina

Domains with local excess of electric charges are expected in most dielectric solids, since these contain charged (as discussed in the case of latex) or polar groups, what accounts for a number of electrical phenomena displayed by them. However, the detailed location and identification of these charged groups is not usually available, and techniques for this purpose are scarce. This situation was alleviated by the introduction of many newer scanning probe techniques, such as the SEPM mentioned above. However, it should be noted that this is just one technique, among many possibilities currently available.

The use of these new electric microscopies has provided very intriguing information, concerning the existence of electrically differentiated supra-molecular domains, in thermoplastic polymer films as well as in inorganic solids. This is evidenced if Figure 4, showing a non-contact AFM and a SEPM picture of alumina, dried from a 0.1% sodium dodecyl sulfate solution. The AFM image does not have any interesting features, but the electric map reveals columnar domains extending for some tens and even hundreds of nanometers, side by side, thus creating large electric potential gradients.

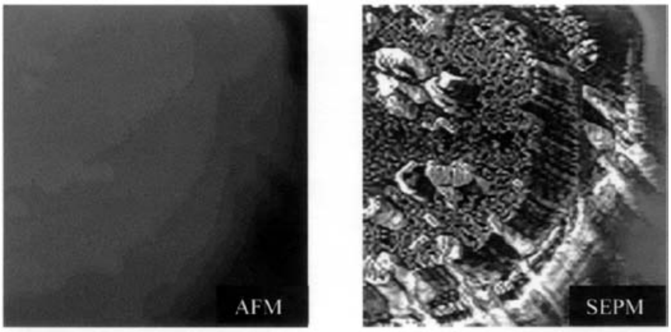

FIGURE 4 Non-contact AFM and scanning electric potential (SEPM) micrographs of alumina particles.

DISCUSSION

There are currently many techniques with powerful microanalytical capabilities, suitable for dealing appropriately with the problem of chemical and electrical heterogeneity of particles and the solids obtained with them. Of course, it is necessary to choose among the many available possibilities, considering the problem addressed and the sample features. No doubt, these techniques are providing us with a wealth of information, unmatched by any other pre-existing procedures.

This is allowing us to better understand some problems in materials fabrication, as we observe the removal of some defects (e.g., in the case of macrocrystals) as the particle samples are fractionated.

The larger variations observed in very small particle populations (diameters measuring tens of nanometers) is a matter of concern, as there is a growing interest in nanoparticles and nanosized structures: when dealing with these materials, we should be aware of the possibility of large variations from one to another particle, which micron-sized particles and structures are averaged-out. On the other hand, in every case examined so far these larger structures are intrinsically heterogeneous, made out of the aggregation of domains with variable characteristics.

The electric potential variations observed in various materials are particularly unexpected, and they show a rich dimension of structural complexity in polymers and colloidal particles which has been all but unnoticed, so far.

Finally, we have many new ways to look at particles and other materials, based on completely different phenomena. The results thus obtained must be compared for mutual validation, or else to reveal inconsistencies. These have to be resolved, either by technical refinement, by improving the interpretation of the raw data, or by formulating new structural hypotheses for the materials under study.

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