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Bicontinuous networks made of polyphosphates and of thermoplastic polymers

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Composite films are obtained by casting aqueous dispersions obtained by admixture of PVAc or styrene–acrylic latexes with aluminium or iron polyphosphate powders. Film extraction with solution of aqueous EDTA (a solvent for polyphosphate) yields a dense polymer film, but using a polymer solvent (chloroform) a porous monolithic solid is obtained. Composite and solvent-extracted films were characterized by SEM coupled to energy dispersive X-ray analysis, and by Raman microspectrophotometry. The results from morphological, spectral and gravimetric experiments show that the cast films are bicontinuous, indicating a strong compatibility of the organic and inorganic phases. This is assigned to ionic bonds at the interfaces, in which aluminium ions act as bridging groups. © 1997 Elsevier Science Ltd.

(Keywords: polyphosphate–polymer composites; polymer latex)

INTRODUCTION

Many polymer materials (composites, immiscible blends and filled polymers) are made out of two or more coexisting phases. In the cases of composites and of filled polymers, many different morphologies are obtained. For instance, the non-polymeric phase may be continuous (e.g. a glass fibre web or tissue used as a thermoset reinforcement) or not (e.g. carbon black or silica used as rubber reinforcing fillers). As a result, one may achieve not only an average or summation of the phases properties but also a synergism among them. Bicontinuous biphasic morphologies have been obtained in the case of polymer blends, e.g. the interpenetrating networks or semi-interpenetrating networks (IPNs or semi-IPNs). Materials made from these networks have attractive physical and chemical properties, for which reason they have continuously received great attention from many researchers[1–6].

In the past few years, we have prepared a number of non-crystalline, non-stoichiometric polyphosphates of aluminium, iron, calcium and other metal ions[7–13]. These are highly versatile compounds, which compositions vary within a broad range. For instance, in the case of aluminium polyphosphate, a large P/Al ratio yields soft glass particles, while a large Al/P ratio is observed in temperature resistant, refractory powers[10].

Using these polyphosphates, we have already obtained gels, including aluminium thermoreversible gels[11,12], glasses and fibres, particles with closed pores[7], self-opacifying particles[8], nanoparticles and cold-formed ceramic-like bodies[13].

We have examined the coating properties of hollow phosphate particles, as well as of dense particles, which undergo morphological transformations within drying latex films.

As we prepared and tested latex paint films filled with aluminium polyphosphate, we observed that these show improved adhesion to glass substrates under wet environments, as compared to conventional paints. Adhesion improvement of coating is a matter of great interest. Its achievement depends on the coating film dimensional stability and on the interactions at the film–substrate interface.

Coating film dimensional stability is an essential factor in determining film adhesion to a substrate, because in the case of film dilation and contraction large stresses are generated at the film–substrate, which finally lead to the joint adhesive rupture. The excellent adhesive performance of the polymer–amorphous polyphosphate films prompted us to examine the morphology and constituent distribution throughout these composite films, which are reported in this paper. We have observed the formation of bicontinuous structures made out of aluminium or iron polyphosphates and either poly(vinyl acetate) or styrene–acrylic copolymers. In this report, we describe the preparation of these networks and we give experimental evidence for their bicontinuous structure.

MATERIALS AND METHODS

Polyphosphate synthesis and analysis

Aluminium (AlPP) and iron (FePP) polyphosphates used in this work are prepared by admixture of sodium polyphosphate, ammonium hydroxide and iron

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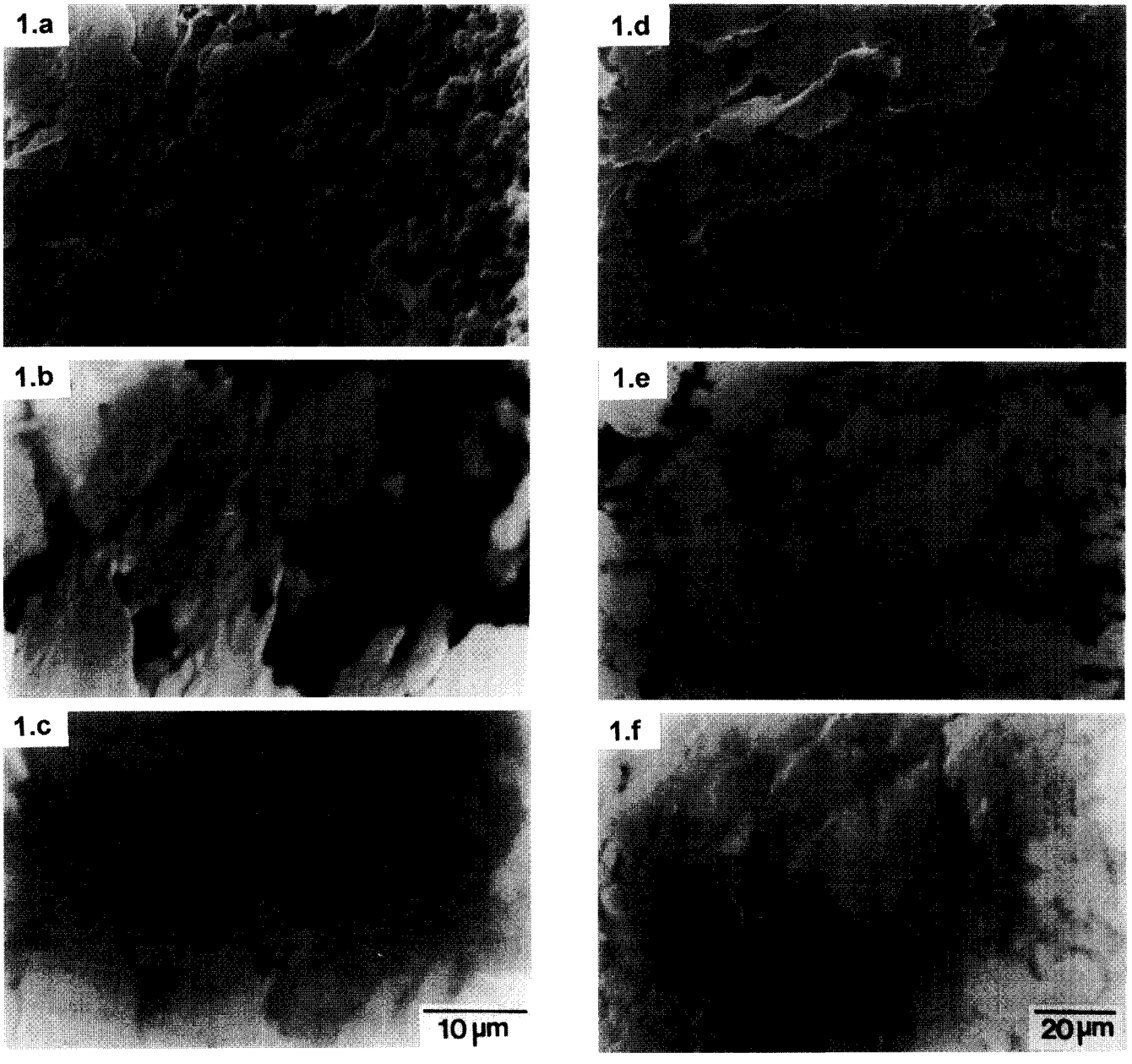


Figure 1 Micrographs of an AlPP/SA film, v_f (AlPP) = 0.4, following extraction with chloroform (a–c) and as cast (d–f). (a, d) are secondary-electron (SEI) images; (b, e) are backscattered-electron images (BEI), composition mode; (c, f) are also BEI images, but in the topography mode

chloride or aluminium sulfate aqueous solutions, followed by centrifugation, drying and milling. Detailed accounts on the preparation and characterization of these substances are presented elsewhere[7,8]. The materials used in this work are from 10-kg pilot scale batches prepared within a joint research program of Unicamp with the phosphate-making Serrana Company.

The phosphorus contents in the aluminium or iron polyphosphates were determined spectrophotometrically by the molybdenum blue method[14] using a u.v./visible Micronal B382 spectrophotometer, with dihydrogen sodium phosphate as the primary standard. Aluminium was determined by complexometric titration with EDTA. Sodium was evaluated by flame photometry using a Micronal B262 flame photometer, with sodium chloride as a standard. Elemental composition was as follows: the AlPP is 25.0% P, 10.9% Al ([Al]/[P] = 0.436) and less than 0.05% Na. The FePP is 26.0% P, 19.5% Fe ([Fe]/[P] = 0.750) and 1.0% Na.

Film preparation and extraction

Films of mixed polyphosphates and polymer latexes were prepared by mixing the latex and polyphosphate powder aqueous dispersions and casting over glass plates. The polyphosphate was first weighted and dispersed in distilled water. This dispersion was added to a definite amount of poly(vinyl acetate) (PVAc) or styrene–acrylic copolymer (SA) latex and the mixture was homogenized using a shearing mixer ('tissue homogenizer'). Then the latex–polyphosphate dispersion was defoamed by immersion in a 25 kHz Thornton GA200 ultrasonic cleaning bath, for 90 s. Finally, the films were cast according to the ASTM D823-87 standard. The dispersion was spread as a paint on glass sheets

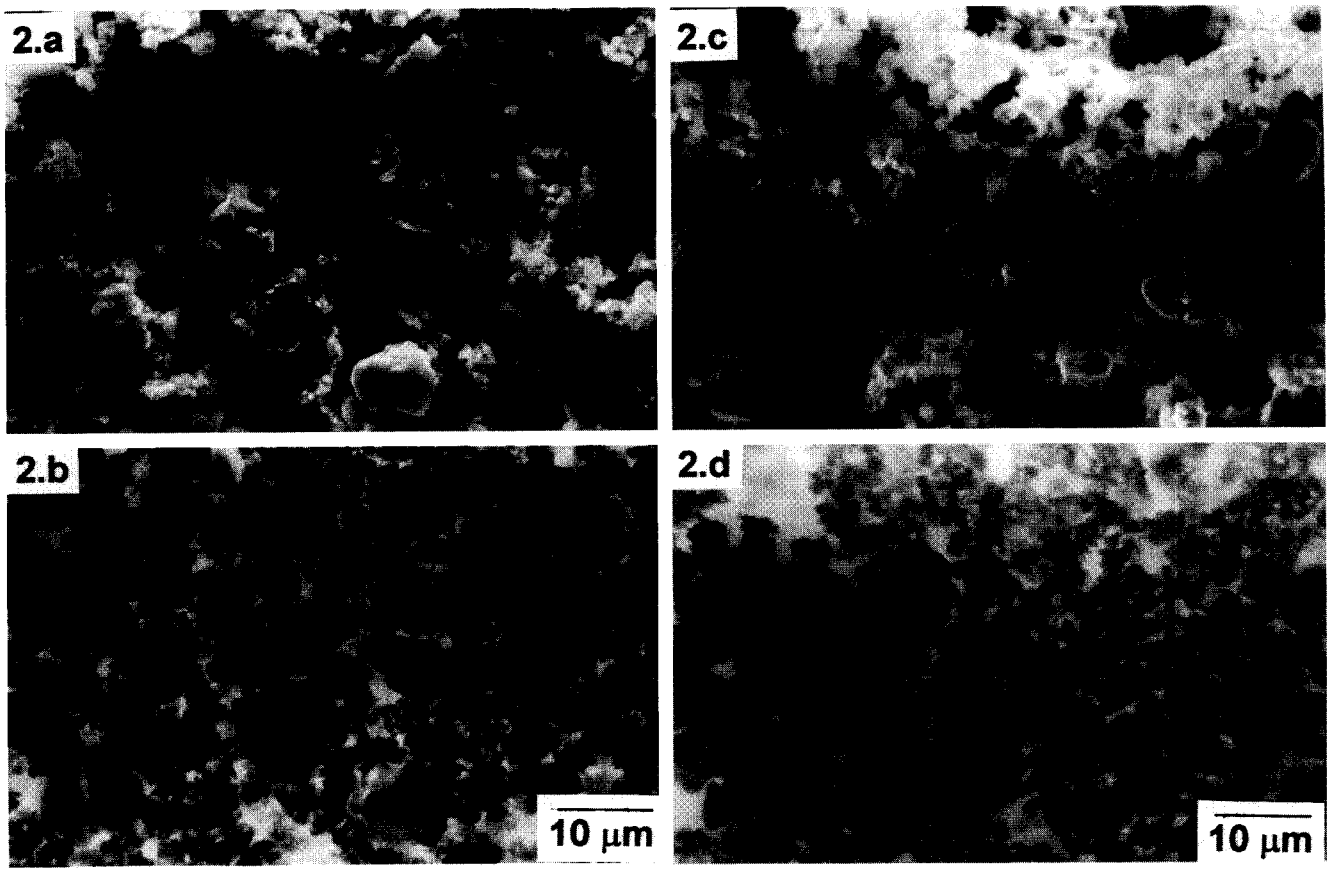


Figure 2 Scanning micrographs of chloroform-extracted FePP/PVAc films. (a, b): v_f (FePP) = 0.8 and (c, d): v_f (FePP) = 0.2. (a, c): SEI; (b, d): BEI

(1 × 25 × 75 mm), previously cleaned and dried. The films were air-dried for at least 12 h before any further analysis. Films were prepared with the total pigment volumetric fractions (v_f) equal to 0.2, 0.4, 0.5 and 0.8, thus covering a broad range of phosphate-to-polymer volume ratios.

Cast films were extracted with aqueous EDTA solutions (which is a solvent for aluminium and iron polyphosphates) or with chloroform, which dissolves the polymers used: PVAc and styrene-acrylic copolymers. Extraction procedure was as follows: each film sample was placed within a closed glass container to which a volume (large enough to cover all the film sample) of the desired solvent was previously added: chloroform, aqueous EDTA solution (0.1 M) or water. After the given extraction period, usually 12 or 24 h, the sample was removed and allowed to dry under air.

Control and extracted films analysis

The film weight loss after each extraction was measured using an analytical Mettler H54AR balance. Scanning secondary and back-scattered electron micrographs (SEM) and the elemental distribution maps were obtained in a Jeol T300 microscope operating at 20 kV, fitted with a NORAN EDS analyser. Samples observed by SEM were detached fractions of the dried films before (control) and after each solvent extraction, fixed on a carbon sample holder and carbon coated. The Raman microspectra of the film surfaces before (control) and after each extraction were obtained with a Renishaw Raman microspectrophotometer operating with a Ar–Ne laser. Optical micrographs of the analysed region of the film surface were obtained with a videomicroscope and directly printed.

RESULTS

Continuous, opaque films are obtained by casting both aluminium or iron polyphosphate–polymer dispersions. The cast films are strongly adherent to glass surfaces.

Film exposure to EDTA solutions leads to the formation of translucent, monolithic, viscoelastic polymer films, similar to the films cast from (unmixed) latex only.

On the other hand, composite film extraction with chloroform leads to the formation of monolithic, brittle and porous polyphosphate films. This means, the removal of the polymer leaves behind a self-sustaining three-dimensional polyphosphate network of macroscopic dimensions. This is unusual, among particle-filled polymer films, and it can only be rationalized assuming that the composite films are bicontinuous networks, from which any of the two continuous phases can be extracted while the other is left essentially undisturbed.

Morphological examination of aluminium polyphosphate/styrene-acrylic (AlPP/SA) latex films

Micrographs of the polyphosphate–polymer composite- and chloroform extracted-AlPP/SA films are presented in *Figure 1*. Three different images are presented, in each case: one is a secondary electron

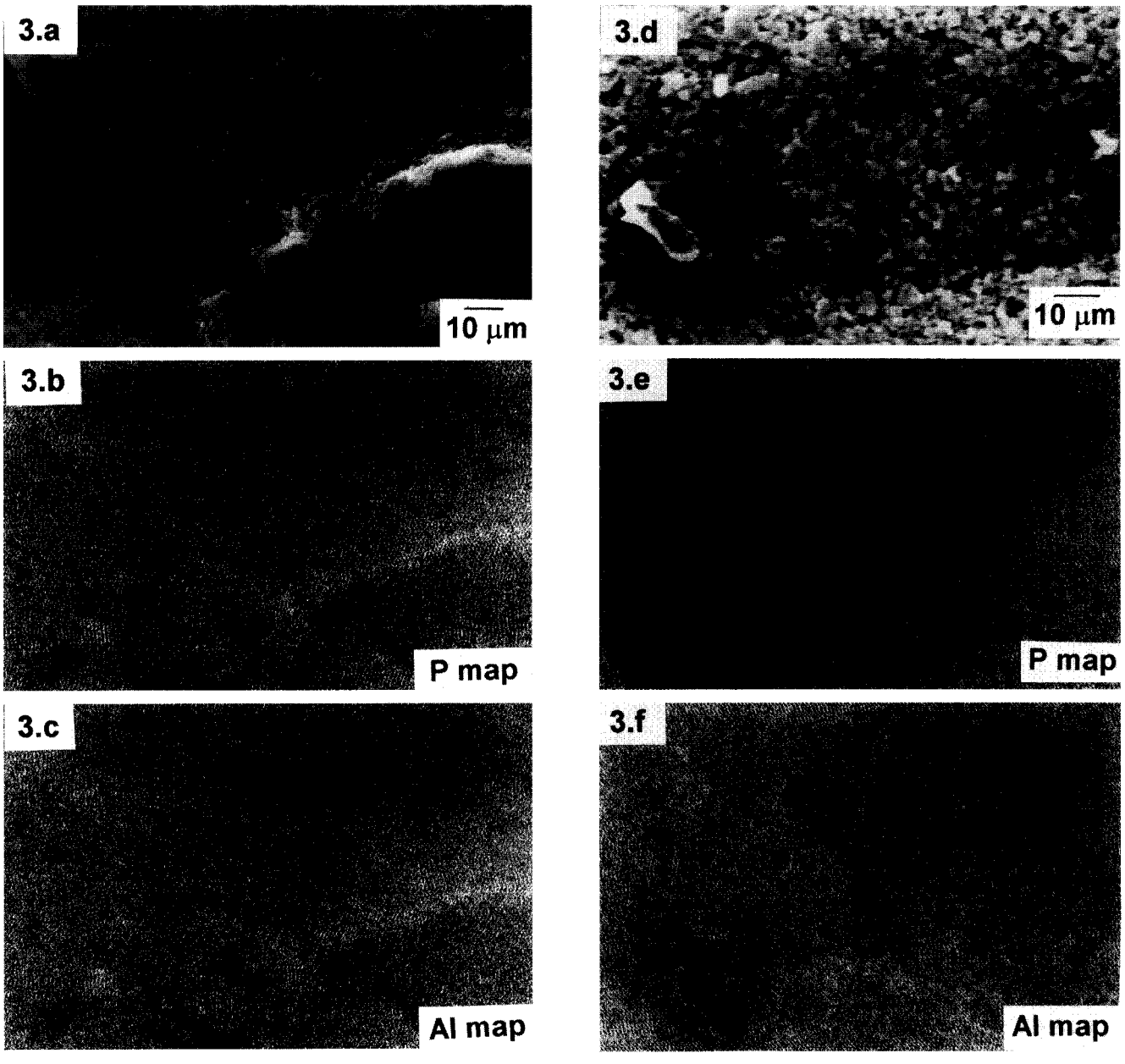


Figure 3 Scanning micrographs and X-ray elemental distribution maps from an AlPP/PVAc cast film, v_f (AlPP) = 0.5, (a–c), and from the same, but following extraction with chloroform (d–f) and aqueous EDTA (g–i). (a, d, g) are SEI pictures

image and the other two are backscattered electron images, in the composition and topography modes. We observe extensive interconnection of the phosphate particles, in both cases.

Beyond that, the comparison of both kinds of BEI pictures of the composite films shows that the phosphate-rich regions are interspersed with polymer. However, in the extracted film the topography is much rougher, evidencing the voids left behind by polymer extraction.

Morphological examination of iron polyphosphate/poly(vinyl acetate) (FePP/PVAc) latex films

Scanning micrographs (SEI and BEI) of chloroform-extracted films, containing v_f (FePP) = 0.8 and 0.2 are presented in *Figure 2*. The percolation of both voids (dark in SEI mode, clear in BEI) and phosphate domains is visible in both cases, but the phosphate domains are smaller in the $0.2\,v_f$ (FePP) film, as expected. Domain surfaces are often finely enmeshed and the width of voids (which correspond to the original polymer domains) is always a few microns, or less, but there are also coarser phosphate domains, some of which have smoother surfaces.

Weight losses under extraction

Weight losses of composite polymer-polyphosphate films were determined, following extraction with EDTA or chloroform. In the case of the AlPP/PVAc films, the amount of material dissolved by EDTA solution corresponds closely to the amount of polyphosphate in the film (e.g. 0.0361 g extracted after 144 h exposure out of a 0.0516 g film sample, containing 0.0361 g AlPP). However, the amount of solid withdrawn by chloroform under very long exposure exceeds the polymer contents of the film (e.g. 0.0313 g withdrawn from a 0.0682 g sample, containing 0.0205 g PVAc). This means, the organic solvent removes the polymer together with some

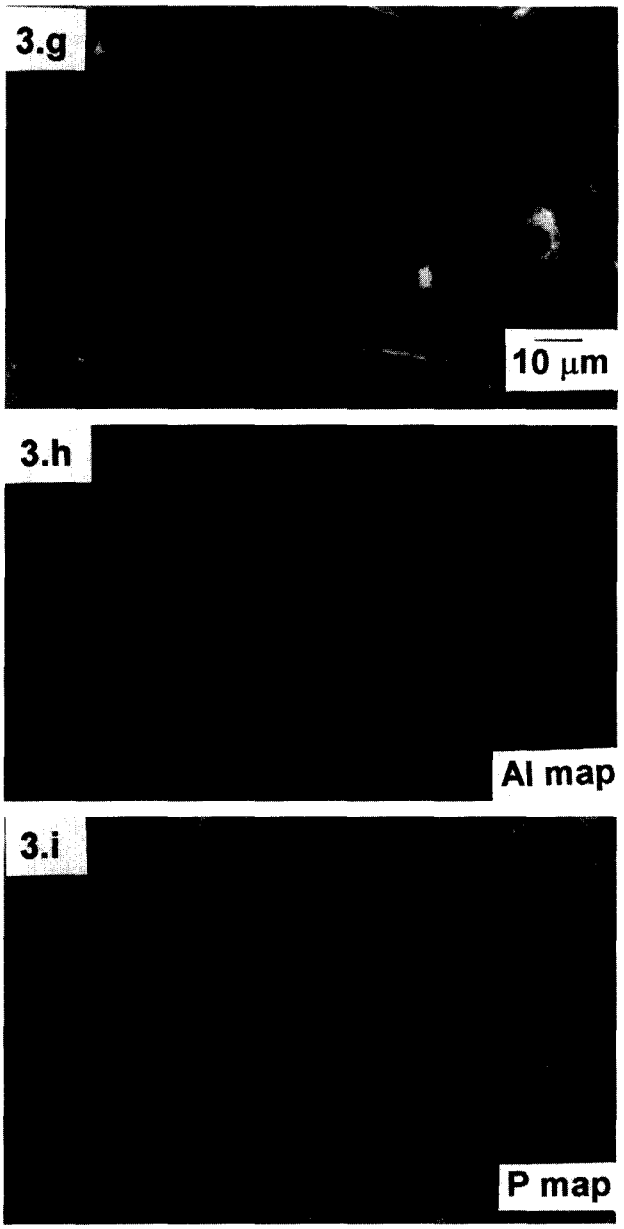


Figure 3 *(Continued)*

particulate polyphosphate, which shows that the polyphosphate network does not fully resist the tensions associated with chloroform swelling, when this is extended for many days.

In the case of FePP/PVAc films, the comparison between polymer contents and weight loss after chloroform extraction shows that polymer removal was almost complete, but iron polyphosphate extraction by EDTA was only partial, in the extraction times used. From these results, we conclude that the polymer phase is fully accessible to solvent, and can be completely dissolved. On the other hand, the inorganic phase is not completely accessible to aqueous solvent, this means, it is mostly continuous but some isolated particles are trapped within polymer domains, and they can be removed only when the surrounding polymer is withdrawn.

Comparison between composite AlPP/PVAc film and the corresponding porous solid

Figure 3 shows micrographs and also the elemental distribution maps from an AlPP/PVAc film, together with films obtained by extraction with EDTA and chloroform. The inorganic phase (P, Al) is distributed throughout the sample, with a fine texture both in the composite film and in the film from which the polymer was extracted. However, in the film extracted with EDTA, some discrete polyphosphate particles are still observed, which indicates that these are less accessible than others. The EDTA-extracted sample is not porous, evidencing the densification of the low-T_g polymeric matrix, concurrent with polyphosphate removal.

Comparison between composite FePP/PVAc film and the corresponding porous solid

Figure 4 presents micrographs and the corresponding elemental distribution maps of FePP/PVAc film and of the films obtained from this one, by extraction.

The results are essentially analogous to the previous ones, with a major difference: the distribution of Fe ions does not follow the distribution of phosphate closely, as in the previous case, evidencing that there are other iron species in this film, beyond iron phosphates. These are probably iron hydrous oxides or hydroxosalts.

Comparison between the AlPP and FePP porous films obtained by extraction of composite films with $CHCl_3$

Scanning micrographs from the surfaces of porous inorganic films obtained by chloroform extraction from both composite AlPP and FePP films are presented in *Figures 3d* and *4d*. We observe that the porous iron polyphosphate solid is much coarser. Considering that the two salt powders used in the film preparation had almost the same granulometric distributions, this shows that the iron polyphosphate particles have a greater tendency towards aggregation, during the storage or even during one or more of the various steps of film preparation.

Raman microspectra of FePP/PVAc films

Raman microspectra were used for domain identification within composite materials. *Figure 5* gives the spectra of iron polyphosphate and PVAc. There is little band superimposition in these spectra, which allows us to identify both components, in the composite films. In *Figure 5*, the wavenumbers assigned to polymer group vibrations are printed in italic, while the polyphosphate wavenumbers are not. This same convention will be used in the next figures, to help the identification of the spectral peaks.

Figure 6a presents an optical micrograph of a composite film surface, in which three domains are marked; the Raman microspectra of these three regions are also presented in the same figure (*Figures 6b–d*). In the darker spot (marked '1' in *Figure 6a*), contributions of both phosphate and polymer are easily detected, in the corresponding spectrum. However, in the clearer spots (marked '2' and '3' in *Figure 6a*) phosphate is prevalent, since the intensity of bands arising from the polymer is low.

We have also obtained spectra of extracted films, which are compared to the spectrum of the composite film, in *Figure 7*. This was done using three different film compositions, respectively v_f (FePP) = 0.8, 0.5 and 0.2. From these spectra, we observe that polymer extraction is essentially complete, with chloroform, since intense polymer bands are not detected in the spectrum. On the other hand, phosphate extraction is not as complete,

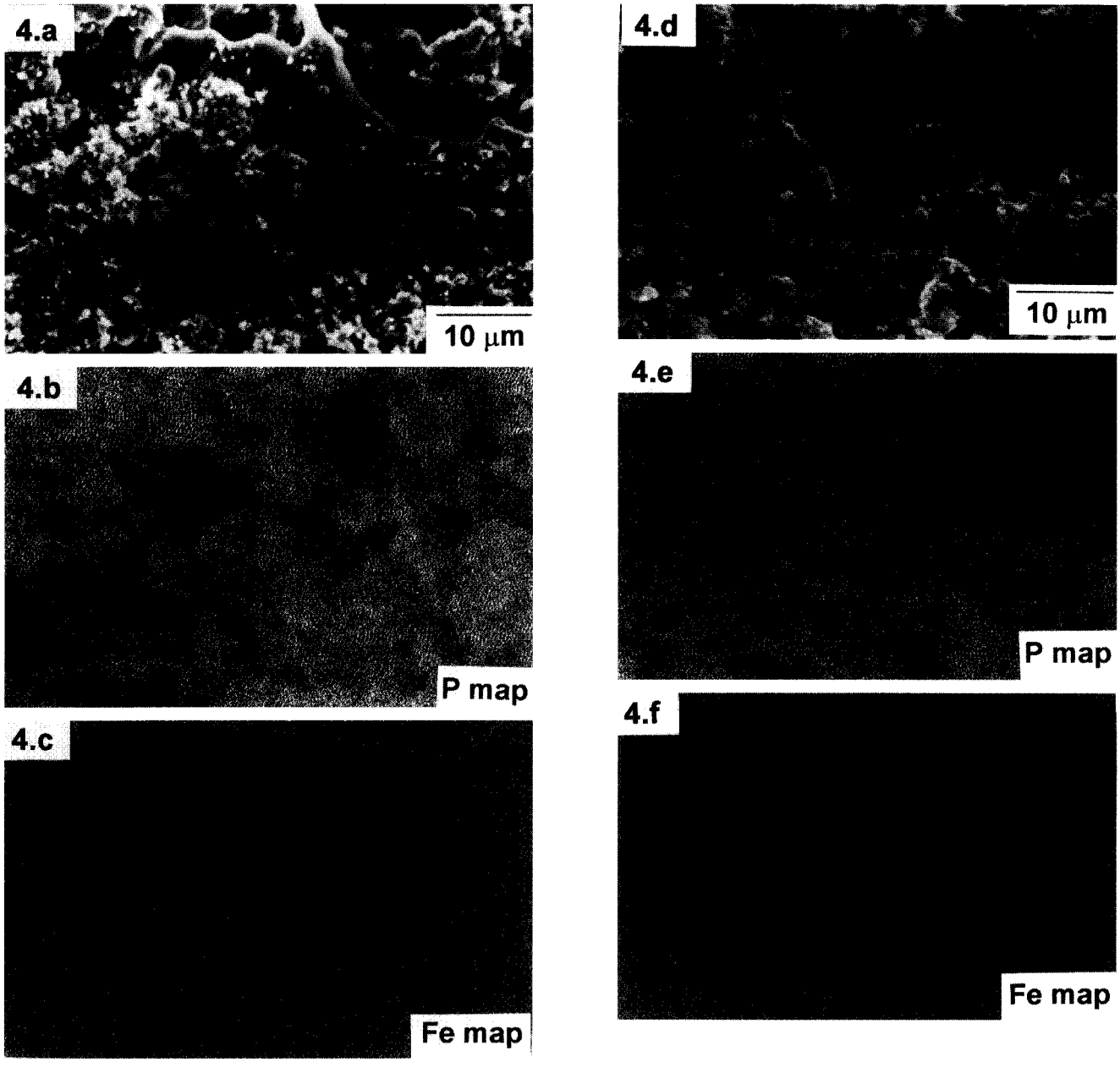


Figure 4 Scanning micrographs and X-ray elemental distribution maps from a FePP/PVAc cast film, v_f (FePP) = 0.5, (a–c), and from the same, but following extraction with chloroform (d–f) and aqueous EDTA (g–h). (a, d, g) are SEI pictures

with EDTA. This effect is very strong in the sample prepared with an excess polyphosphate, from which the Raman spectrum is still dominated by a phosphate band at 1020–1080 cm^{-1}, even after extraction with EDTA. However, PVAc removal with chloroform is always complete, as judged by the residual peak intensities.

This confirms the results from electron microscopy and from the gravimetric determinations, concerning the degree of completeness in the removal of each phase, by extraction.

DISCUSSION

All the results presented in this work can be understood assuming a simple model: polymer latex particles associate with polyphosphate particles, and this association is mediated by the trivalent aluminium and iron ions, which bind to negative latex surface groups. As the phosphate–polymer film dries, both phases are strongly interconnected by water resistant, electrostatic phosphate–aluminium (or iron)–sulfate (or carboxylate, or sulfonate) bridges.

According to this model, two highly immiscible phases are rendered compatible by the association between negative charges from polymer surfaces and positive charges from the polyphosphate. Due to the resulting low interfacial tension, extensive interfacial contact is allowed, which in turn allows the formation of a bicontinuous network.

Ionic Al^{3+} (or Fe^{3+})–bridges can also account for enhanced film binding to the negative glass surfaces.

The importance and effectiveness of ionic bridges in the stabilization of supramolecular structures is well documented in the literature, in the cases of ionomers, of polyelectrolyte gelation[15] and of polymer-particle binding, in flocculation.

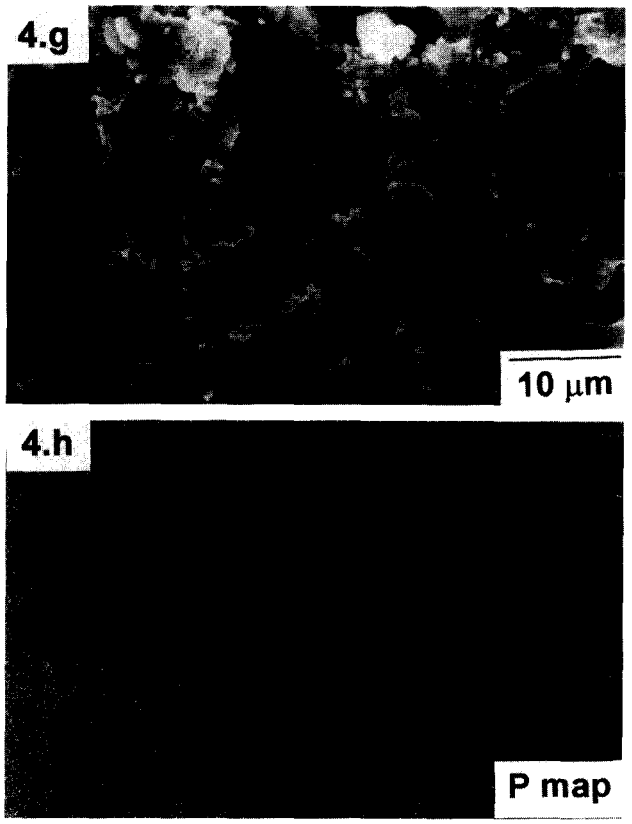


Figure 4 *(Continued)*

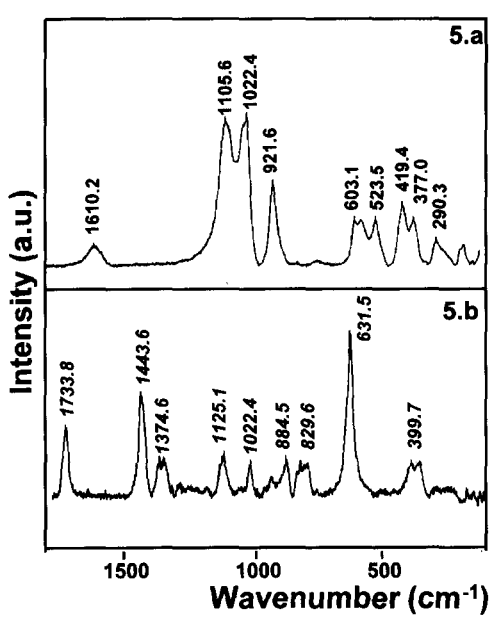
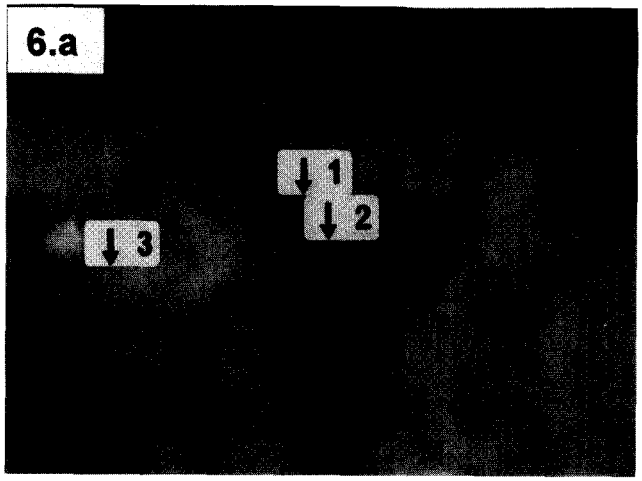


Figure 5 Raman microspectra of iron polyphosphate (a) and of PVAc (b)

Gravimetric, morphological and spectroscopical data presented in this work are consistent with the description of the polymer–polyphosphate films as strongly interpenetrating, bicontinuous networks. The preparation of monolithic solids by extraction with both chloroform and aqueous EDTA shows that the two immiscible phases percolate throughout the volume of the composite.

The polymer phase is completely accessible to solvent,



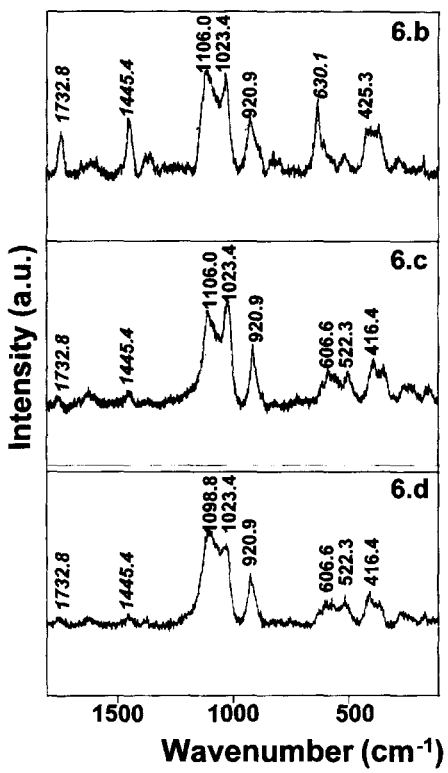
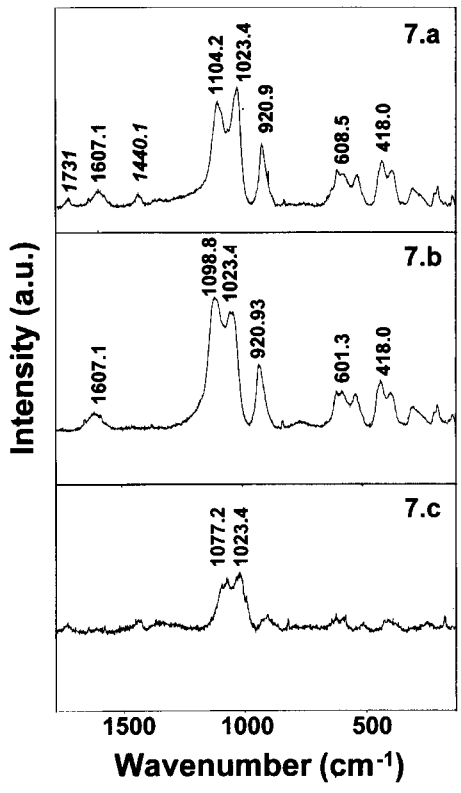
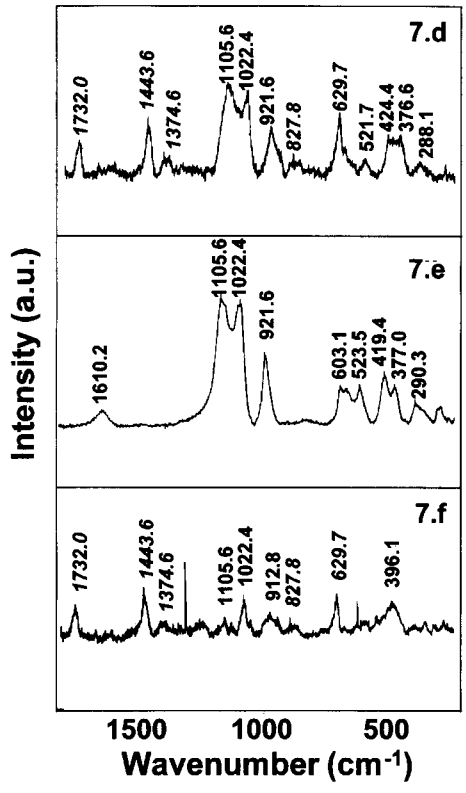


Figure 6 Optical micrograph of FePP/PVAc cast film surface, v_f (FePP) = 0.5, (a) and Raman microspectra of the three spots marked in (a): (b) is from spot 1, (c) from spot 2 and (d) from spot 3

and its removal by extraction is fairly complete even when this is the minority component, leaving behind a phosphate skeleton. On the other hand, the inorganic phase is not as completely extracted which shows that some particles do not belong to the continuous network, but are surrounded by polymer. This is observed even in the sample in which latex polymer is the minority component, and probably arises from an imperfection in the mixing procedure, or perhaps from the result of particle heterogeneity, in the sample used. However, the behaviour of the polymer–polyphosphate films should be strongly contrasted to the behaviour of polymer films filled with independent particles (such as titanium oxide, calcium carbonate or kaolin), which do not associate themselves to make a tridimensional network within the polymer film. In these cases, exposure of a particle-filled





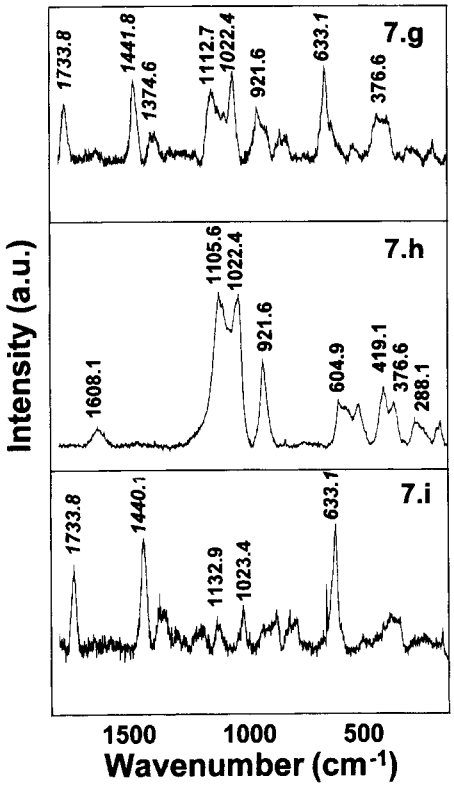


Figure 7 Raman microspectra of composite FePP/PVAc cast film surface. v_f (FePP) are: (a–c): 0.2; (d–f): 0.5 and (g–i): 0.8. In each case are given the spectra of the composite film (a, d, g), the $CHCl_3$-extracted film (b, e, h) and the EDTA-extracted film (c, f, i)

polymer film to a polymer solvent does not produce any inorganic monolith, as observed in this work. A particle dispersion within a polymer solution is obtained, instead.

A question arising is the following: if the trivalent ions are as effective in improving latex film adhesion to surfaces, why are they not used more often? From a colloid chemistry point of view, there is a simple answer to this question: these ions are powerful coagulants, and their addition to latex is likely to impair both latex stability and film-forming abilities. In this respect, the polyphosphate particles may be seen as a way to feed trivalent cations to the latex, but in a strongly sequestered state, so that they do not act as coagulants.

If this model and the arguments used in this work prove valid in other cases, the polymer–polyphosphate networks may become effective solutions for many problems of poor coating and phase adhesion, under wet environments.

CONCLUSION

Bicontinuous polymer–phosphate interpenetrating networks are formed by casting films from phosphate–latex dispersion. Network formation and stability as well as the observed phase compatibility are interpreted as the result of ionic (aluminium or iron to sulfate, carboxylate or phosphate) binding at the polymer–phosphate particles interface.

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