

Preparation and Properties of Poly(acrylic acid)-Based Hybrid Compounds

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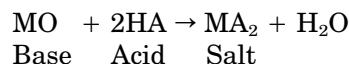
ABSTRACT: Hybrid organic–inorganic materials were prepared by using two different zinc salts and poly(acrylic acid) (PAA). The characterization of the resulting compounds show that polymerlike materials with a decomposition temperature above 673°C can be produced and that the specific zinc salt and synthesis route influence the final properties of these materials. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 861–868, 1997

INTRODUCTION

Polyelectrolyte-based cements and compounds have attracted a great deal of attention^{1–7} since they were first synthesized in the late 1960s.⁸ Besides the purely scientific interest, these materials are particularly relevant for practical applications because of their standard use as dental restoring or filling elements^{1–18} and also because they represent a kind of hybrid organic–inorganic material. Another interesting aspect of polyelectrolyte cements is their low-temperature synthesis requirements, which represents an exciting opportunity for producing novel materials by combining ceramic or metal elements with macromolecular substances, which normally decompose above 373 K.¹³

One of the most studied polyelectrolyte-based systems is the reaction of poly(acrylic acid) (PAA) with divalent metal oxides (probably ZnO is the most common one). The experimental evidence leads one to think that, in this case, the compound is formed through the reaction of the metal cations

with the carboxylate anions of PAA. The divalence of cations allows them to react with carboxyl groups of neighboring chains of the PAA, thus forming a crosslinked three-dimensional structure. Therefore, these materials can be described as acid–base reaction products, since the reaction product is a kind of salt which acts as a matrix. Schematically, the reactions has been represented as



where MO stands for the metal oxide, and HA, for the polymer.

Studies of a number of such systems indicate that there exist various stages for the corresponding reaction.¹⁹ First, the metal oxide powder is partially decomposed by the polyacid, and cations are liberated. Then, during the formation of the cement, more cations are formed and transported due to the diffusion of the liquid polymer into the powder particles and the acid–base reaction takes place, forming a hydrogel, with interesting mechanical properties which, as mentioned, have found practical applications in dentistry and in

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the biomedical field, due to the good biocompatibility and adhesion of these compounds.

According to the literature, ion diffusion is one of the driving mechanisms for the reaction of these hybrid compounds, which has important consequences on the final properties. Indeed, FTIR experiments^{12,15} have demonstrated that there exists a minimum molar relation MO/PAA required to consume all the available carboxyl groups. This minimum value ($=1.0$) is well above the theoretical stoichiometry of the MO–PAA reaction ($=0.5$), which indicates that not all the metal oxide reacts completely, due to the particle size. This means that the microstructure of such compounds is formed by a matrix of the hydrogel with unreacted metal oxide particles embedded, as microscopy and X-ray diffraction studies have shown.^{13,15,20} Therefore, all the previously reported polyelectrolyte-based compounds are really partially reacted systems, which explains some of the controversy on the viscoelastic properties and durability of these materials, since the properties depend on the particle-size distribution of the metal oxide phase, as well on the presence of traces of other ions, such as magnesium and calcium.²⁰

In this present contribution, instead of following a solid state (i.e., the metal oxide powder)–liquid state (i.e., the PAA) synthesis route, an alternative methodology, by using a liquid–liquid approach, is presented. Two zinc salts, $ZnCl_2$ and $Zn(CH_3COO)_2 \cdot 2H_2O$, were studied, when reacting with PAA, and the corresponding properties characterized.

EXPERIMENTAL

Materials

Poly(acrylic acid) (PAA, Aldrich), with a molecular weight of 90,000 and $T_g = 400^\circ C$, was used in an aqueous solution with 25% solids content. Zinc chloride (Baker) with 99.1% purity and with a pH of the solution of 5.8 (measured at 5% concentration at 298 K) was employed for preparing one set of specimens, whereas another different set of samples was prepared from zinc acetate (Baker) of 100% purity with a pH of the solution of 6.4 (measured at 5% concentration at 298 K). For both salts, 0.1N aqueous solutions were prepared for the reaction with PAA.

Synthesis Routes

Two methods were devised for preparing the zinc salts–PAA compounds.²¹ Figure 1 shows sche-

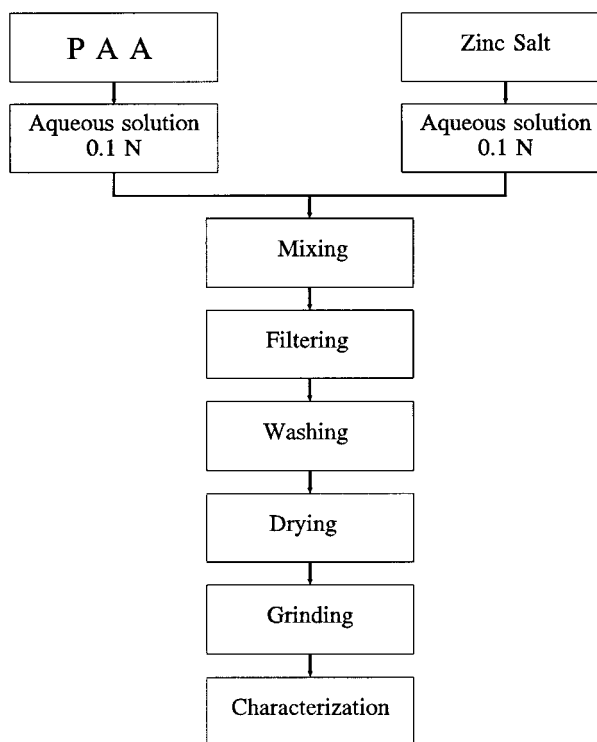


Figure 1 Schematic representation of the gel method for preparing the zinc acetate–PAA compounds.

matically the so-called gel method employed for the zinc acetate. The reaction in this case was carried out at room temperature under constant stirring, producing a gel which was then washed with distilled water and dried at 348 K for 24 h. Since the zinc chloride did not produce a solid phase when reacting with PAA by the method depicted in Figure 1, a sodium salt was prepared as schematically described in Figure 2. In this case, the result was a precipitate which was washed with distilled water and dried at 347 K for 24 h. A third family of samples was prepared by the precipitate method, but now using zinc acetate. Table I summarizes the whole set of samples prepared, along with the corresponding salt/PAA molar relationship.

Characterization Techniques

Atomic absorption spectrometry (Varian AA-175) was employed for determining the zinc concentration in the materials produced, by using an air-acetylene flame. FTIR studies were carried out in a Nicolet 5PC spectrometer in the range 4000 to 300 cm^{-1} , with a resolution of 4 cm^{-1} and by using 32 scans. The samples of both the gels and the

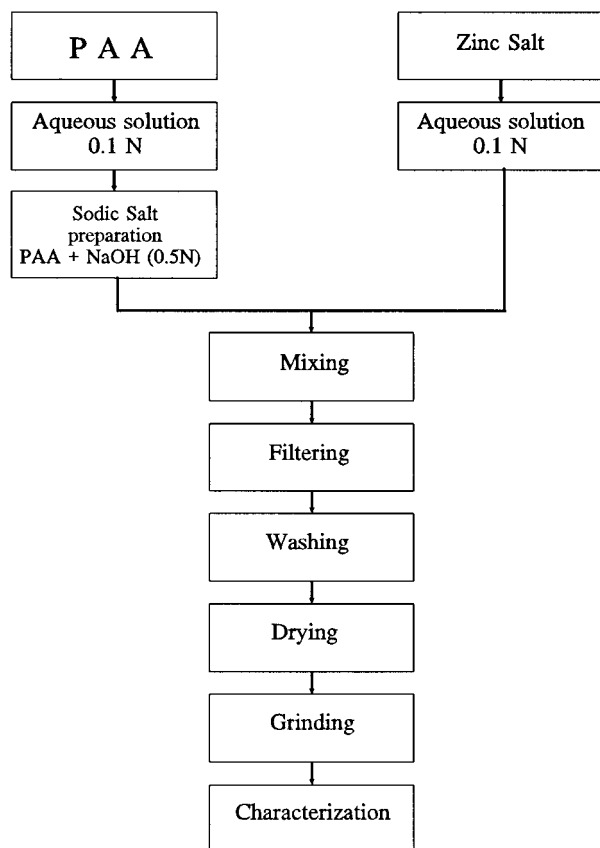


Figure 2 Schematical representation of the precipitate method for preparing the zinc acetate-PAA compounds.

precipitates were powdered in an agate mortar and mixed with KBr (1 : 100 relation) to form a tablet by using a pressure of 5500 psi. A FT-Raman spectrometer (Nicolet 910=, equipped with a YAG-Nd infrared laser (1064 nm), was also utilized for characterizing the powdered specimens. X-ray diffraction was done in a Siemens D500 appara-

Table I Summary of Samples Prepared

System	Sample	Salt/PAA Molar Relation
Zn(CH ₃ COO) ₂ /PAA	1	0.5 (stoichiometry)
	2	0.75
	3	0.25
Zn(CH ₃ COO) ₂ / (PAA + NaOH)	4	0.5 (stoichiometry)
	5	0.75
	6	0.4
ZnCl ₂ /(PAA + NaOH)	7	0.5 (stoichiometry)
	8	0.75
	9	0.4

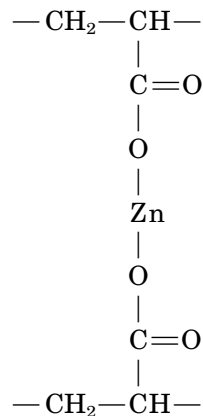
Table II Atomic Absorption Results

Sample	Salt/PAA Molar Relation	% Zinc
1	0.5	20.97
2	0.75	24.07
3	0.25	22.05
4	0.5	25.93
5	0.75	26.73
6	0.4	22.94
7	0.5	25.51
8	0.75	28.31
9	0.4	24.83

tus with a rotating copper anode at a voltage of 30 kV. TGA analysis was performed in a DuPont 951 instrument, for samples with a weight of 18 g, at a heating rate of 10 K/min under a nitrogen flux of 50 mL/min. The SEM micrographs were obtained in JEOL JSM-5200 machine at 25 kV in a secondary electron mode, for gold-covered samples, to diminish charging effects. Finally, TEM experiments were carried out in a JEOL-100 CX microscope at 100 keV in bright-field conditions, for uncoated powdered samples deposited on 100 mesh Cu microscope grids.

RESULTS AND DISCUSSION

Table II contains a summary of the atomic absorption results. As explained before, the elemental composition provides an important clue on how much metal has been incorporated into the reaction product. The theoretical zinc content in the final compound can be easily calculated from the expected chemical structure:



Since the molecular weight of this structure is 207.495 and the atomic weight of zinc is 65.38, the

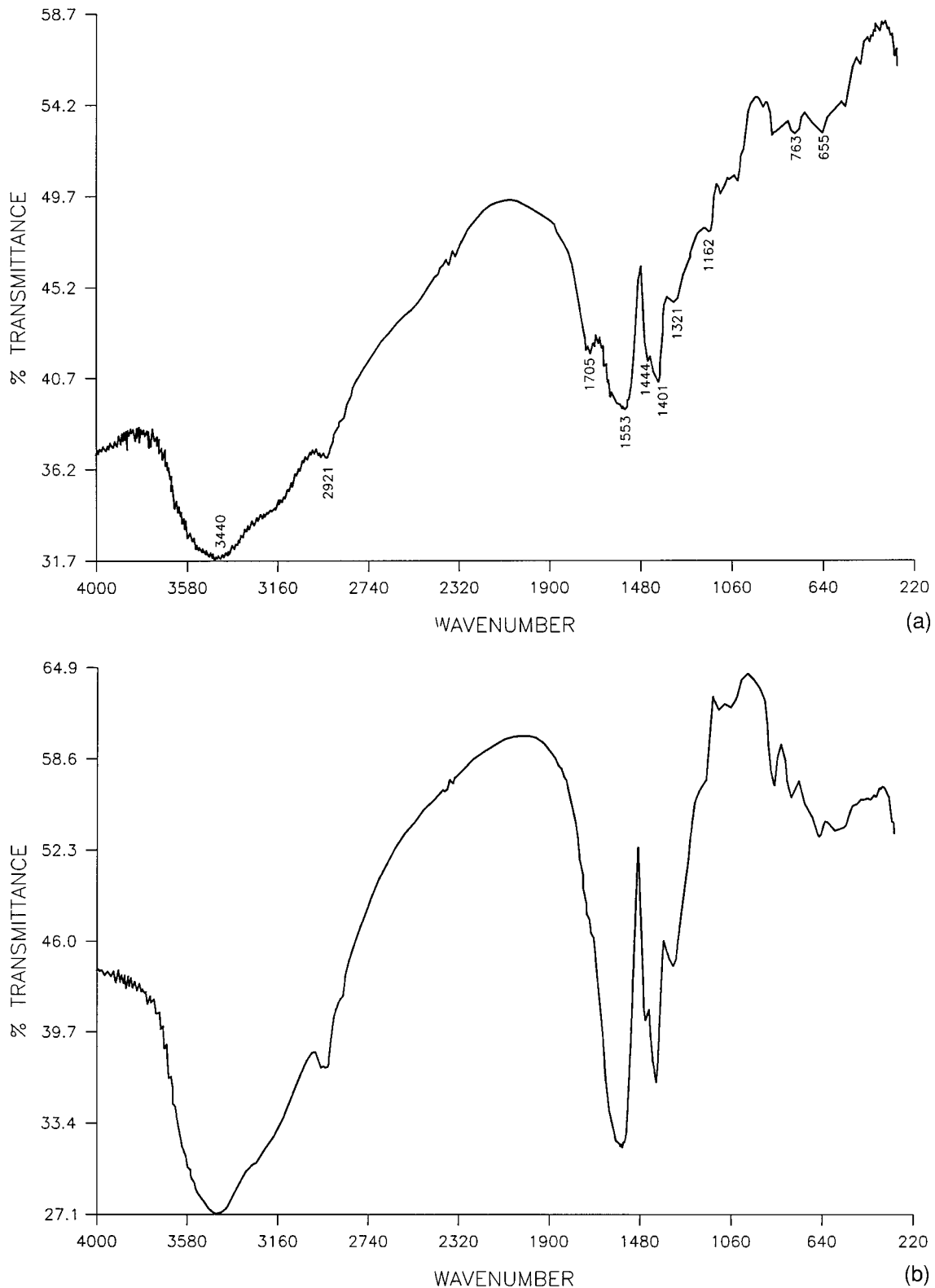


Figure 3 FTIR spectra of (a) sample 1 and (b) sample 9.

expected percentage of zinc in the final structure corresponds to 31.51% of the total weight. From Table II it can be concluded that the samples pre-

pared by the precipitate method produce the highest reaction degree. Some experiments were performed in which higher drying temperatures, up

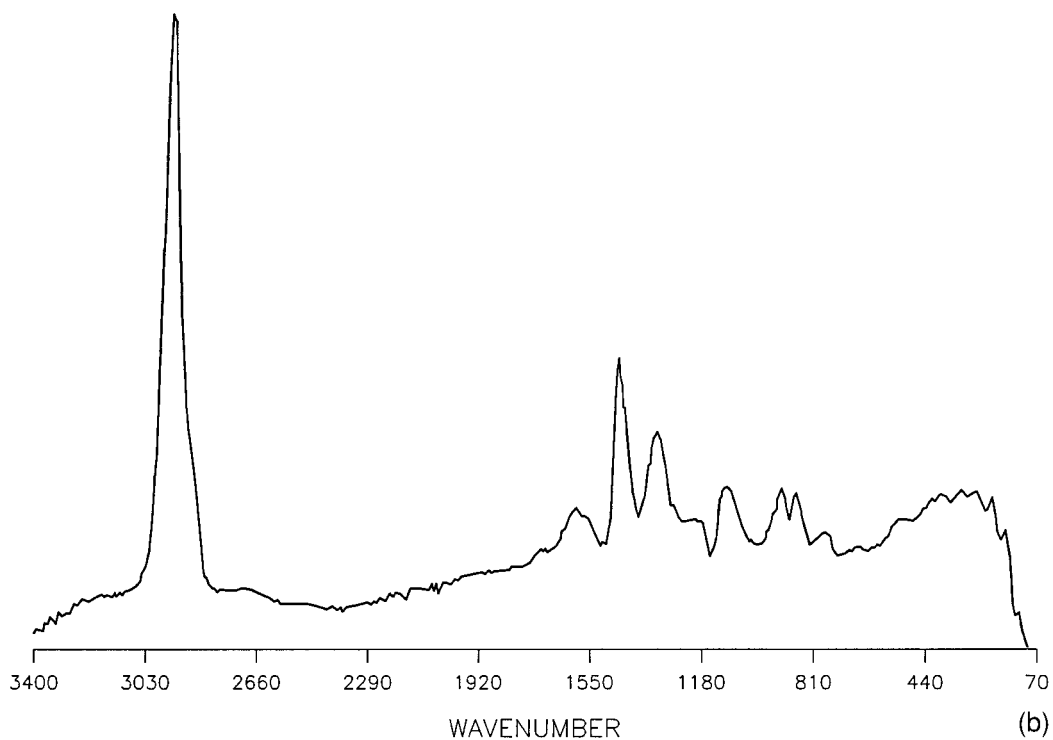
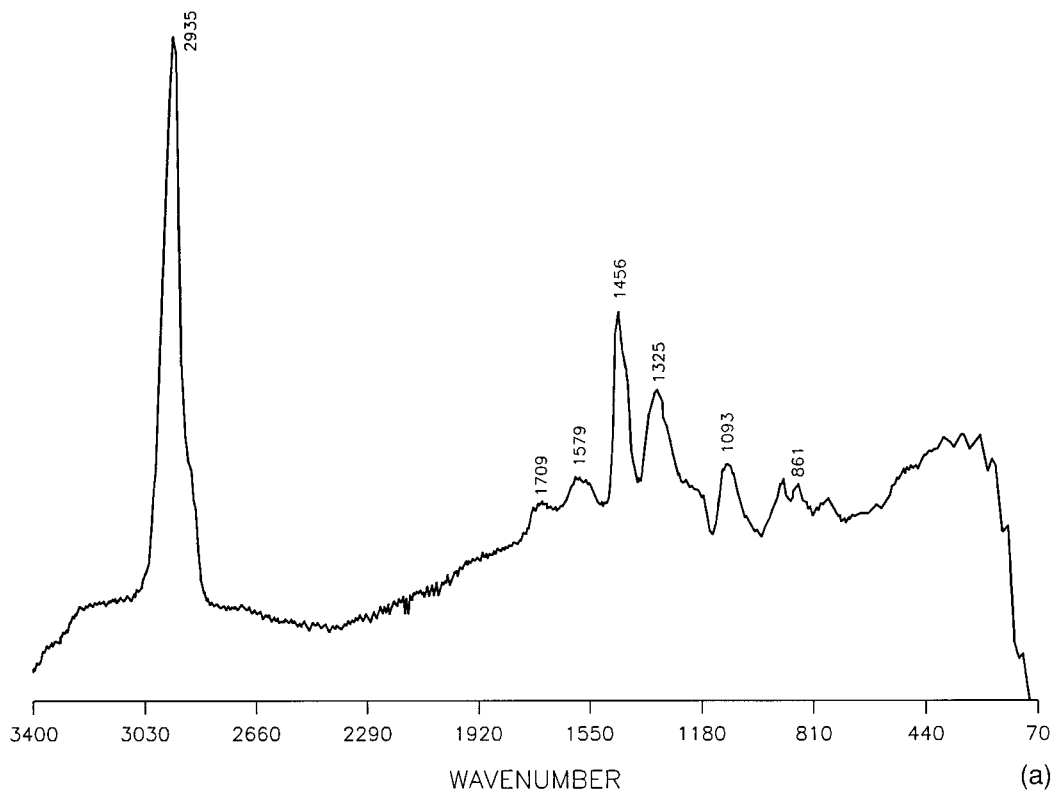


Figure 4 FT-Raman spectra of (a) sample 1 and (b) sample 9.

to 423 K, were used, indicating that, as expected, the amount of zinc incorporated reached 31.5%, i.e., basically the theoretical value. However, a

PAA excess in the specimens produces lower Zn incorporation, since a dissolution (i.e., the inverse reaction) begins to take place. Also, it is worth

Table III TGA Results of the Samples Prepared

Sample	First Peak of Derivative (K)	Second Peak of Derivative (K)
1	699.15	716.15
2	700.15	717.15
3	697.15	717.15
4	702.15	714.15
5	704.15	719.15
6	700.15	—
7	—	715.15
8	705.15	721.15
9	695.15	704.15

mentioning that the amount of Na present in the samples was never higher than 0.56%, indicating that the exchange of ions is extremely efficient.

Figure 3(a) and (b) corresponds to the FTIR spectra of samples 1 and 9, respectively, chosen as examples of the whole set of specimens prepared. As observed there, the general trend is that the stretching C=O band (1719 cm^{-1}) of the carboxyl group is shifted toward smaller wavenumbers and splits into two bands, one corresponding to the symmetrical vibration of COO—, and the other, to the asymmetrical one.^{12,22} This is an indication of the crosslinking reaction. In the samples prepared by the gel method, the characteristic band at 1710 cm^{-1} is clearly seen, indicating that very rapid hardening of the gel does not allow an

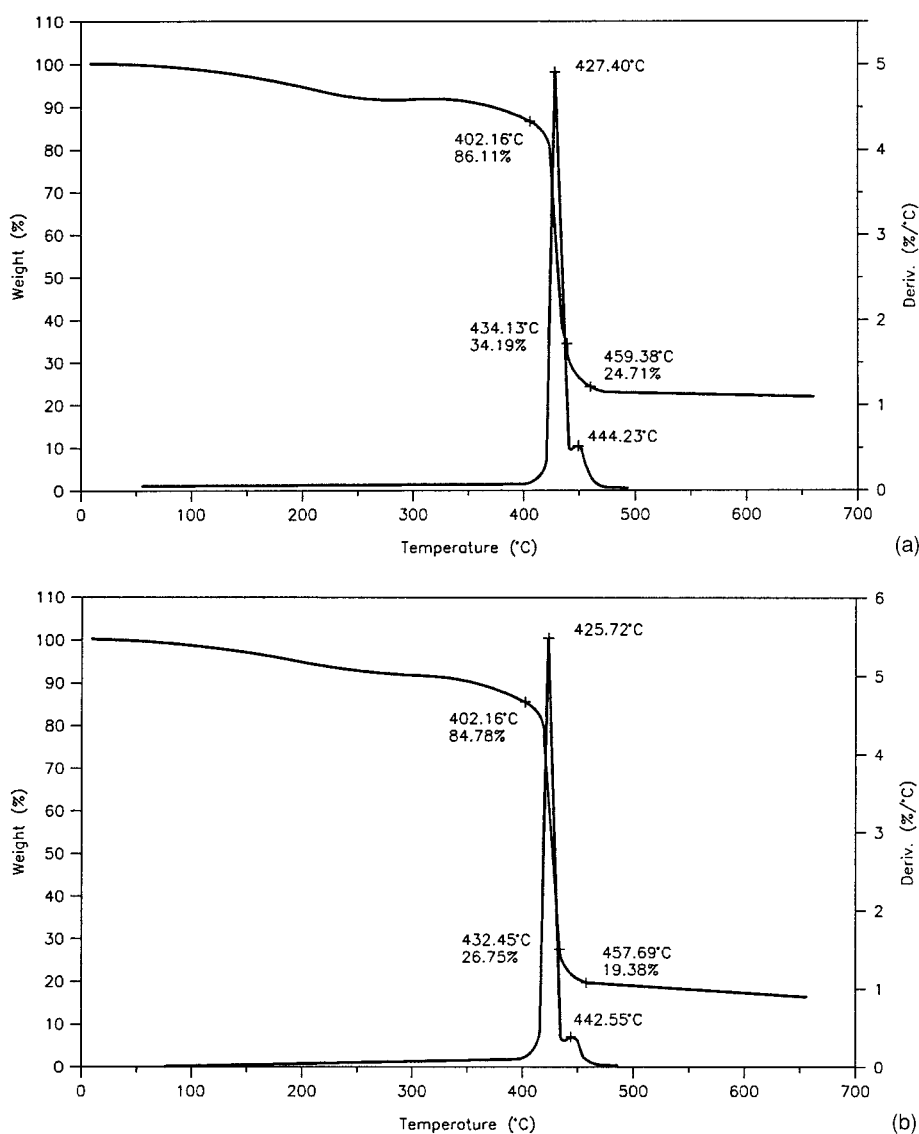


Figure 5 TGA thermograms and their derivatives of (a) sample 1 and (b) sample 9.

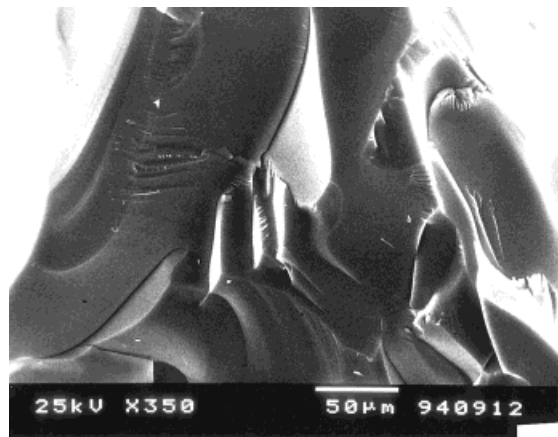
adequate diffusion of ions to complete the reaction. On the other hand, the kinetics of the samples prepared by the precipitate method is much slower and allows a better reaction of the COOH— group. This is in agreement with the atomic absorption results.

The lack of bands at 1256 and 1169 cm^{-1} in the PAA—zinc salts compounds is due to the loss of hydrogen bridge bonds between O—H and C=O groups, indicating the reaction with the salts. These results show that the cations in the solution migrate to the polyelectrolyte phase to react with the polyionic chains. Moreover, according to the literature,²² the C—O $\Delta\nu$ values ($\Delta\nu = \nu_{\text{symmetrical}} - \nu_{\text{asymmetrical}}$) indicate that the most likely structures of the compounds are either the so-called complex bridge or the bidentate chelate.

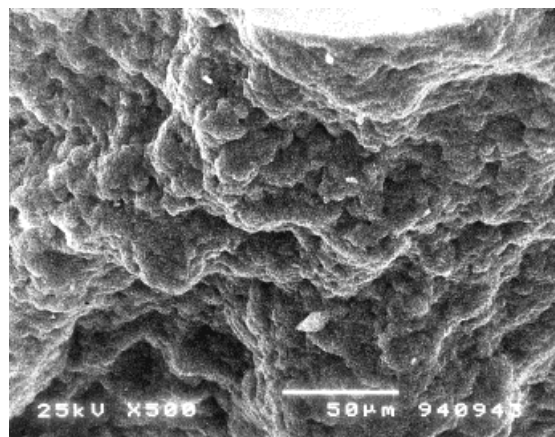
Figure 4(a) and (b) shows the FT-Raman spectra for samples 1 and 9, respectively, which represent the whole set of specimens prepared. Again, the evidence of the reaction of the zinc cation is clear, since the 1709 cm^{-1} band of the C=O group of the COOH, shifts to 1580 cm^{-1} , which corresponds to the C=O group of the COOZn.²² In samples prepared by the gel method, the 1709 cm^{-1} band is stronger than in the case of compounds prepared by the precipitate method, indicating the better reaction in the latter. The Raman results corroborate the FTIR interpretation described. The X-ray results show basically an amorphous material with very little crystallinity, especially for the cases where the reaction was not completed.

TGA results are summarized in Table III, where the temperatures of the two peaks of the derivative of the thermograms are listed. Figure 5(a) and 5(b) shows typical thermograms and their corresponding derivatives of the TGA analysis of samples 1 and 9, respectively. It is interesting to comment on the two peaks of the derivatives, which are always found in the samples, with the exception of samples 6 and 7 (see Tables I and III), which had only one peak. Indeed, the two peaks indicate that the process takes place through two different kinetics. Moreover, samples prepared by the gel method showed more unreacted PAA than did those prepared by the precipitate method, and the more Zn incorporated in the compound (see Table II), the more stable the final material. Nevertheless, the thermal stability of all samples up to temperatures above 673 K is remarkable, showing that an interesting polymer-based material is capable of enduring high temperatures.

The SEM analysis of the fracture surfaces of



(a)



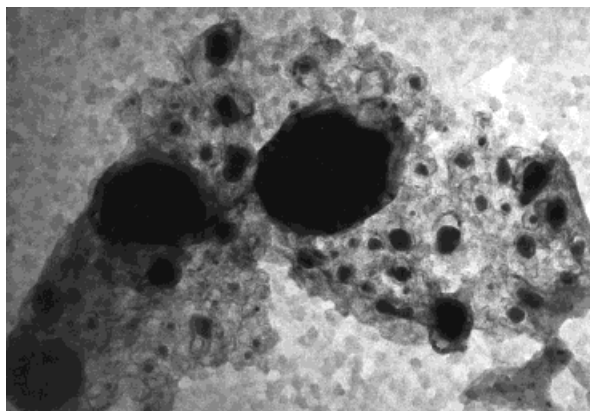
(b)

Figure 6 SEM micrographs of samples prepared by (a) the gel method and (b) the precipitate method.

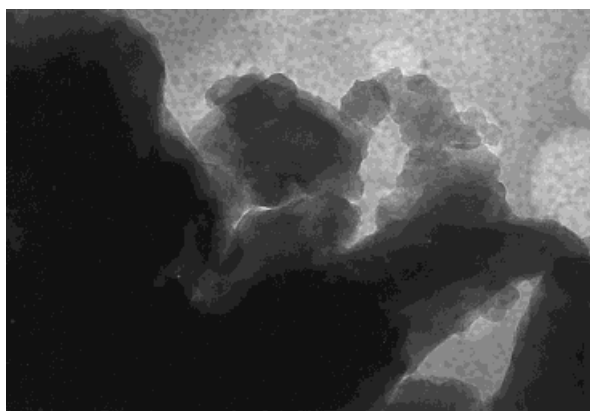
the specimens also showed interesting differences among samples by the two synthesis routes: Whereas the samples prepared by the gel method showed a brittle structure, typical of a polymer gel, as observed in the micrograph of Figure 6(a), the samples prepared by the precipitate method have a globular structure, as seen in the micrograph of Figure 6(b), with a higher surface area and higher homogeneity than in the gel case. Finally, the TEM observations confirmed the results obtained with the other techniques, since the gel method produced tiny oxide particles embedded in the reaction products, as seen in Figure 7(b), whereas the precipitate method produced highly homogeneous materials, as observed in Figure 7(b).

CONCLUSIONS

From the results obtained, it can be concluded that the precipitate method allows one to produce



(a)



(b)

Figure 7 TEM micrographs of samples prepared by (a) the gel method and (b) the precipitate method.

better compounds than does the gel method, due to the slower kinetics involved. Zinc acetate is cheaper, nontoxic, and less hygroscopic than is zinc chloride, which makes it more adequate for handling and for producing good materials. The molar relation of PAA–Zn salts plays an important role in the characteristics of the final products. The results also show the feasibility of producing materials capable of enduring high temperature, despite being prepared at room temperature. Dielectric response characterization¹⁶ indicates that some of the compounds described here present ionic conduction, which, along with the properties presented, open up exciting possibilities for producing hybrid materials.

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