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Research Paper

Preparation and microstructure of cobalt(III) poly (acrylate) hybrid materials

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Abstract

The chemical reactions between poly (acrylic acid) and cobalt (III) oxide and between poly (acrylic acid) and cobalt (III) fluoride were studied by Fourier Transform Infrared Spectroscopy. The results demonstrate the formation of cements between the metal and PAA aqueous solutions. Structural information was obtained from the observed frequency shifts of the absorption bands of the carboxylates groups in the cobalt (III) poly (acrylate) relative to those recorded for the purely ionic form. The results show that the bidentate bridging structure is the most likely to occur in both cases. Also, from the analysis of the corresponding coordination chemistry, an octahedral structure may be tentatively assigned to the cobalt (III) poly (acrylate).

Keywords: *Polyelectrolyte Compounds; Hybrid Materials; Polyacrylic Acid; Cobalt Compounds; Nanocomposites.*

1. Introduction

Poly(acrylic acid) (PAA) and its salts have been known to have useful binding properties for many years. This salts, and poly(acrylic acid) have been used for soil consolidation and as flocculating agents. When poly(acrylic acid) is used for soil consolidation, one is basically just employing one among the vast range of acid-base phenomena, which occur throughout both inorganic and organic materials. Just like Portland cement, the above materials are prepared by mixing a powder with a liquid. However, in the case of PAA-based cements, this liquid phase is not water but an acid, while the powder, a metal oxide, is a base. Not surprisingly, the cement-forming reaction between them is extremely rapid and a hardened mass is formed within minutes of mixing. The product of the reaction, the binding agent, is a complex salt. Each cement system is a particular combination of an acid and a base. Cement-forming liquids are strongly hydrogen-bonded and viscous. They must have sufficient acidity as to decompose the basic powder and liberate cement-forming cations, and they must act as a medium for the reaction. Generally, cement-forming liquids are aqueous solutions of inorganic or organic acids. These acids could be phosphoric acid, carboxylic acids and others. The bases are oxides and hydroxides of di and trivalent metals, some glasses, etc.

The setting reaction for the great majority of acid-base cements take place in water. Water thus acts both as a solvent and as a component in the formation of these cements. Also, it is one of the reaction products, being formed in the neutralization reaction as the cements set.

This kind of cements are not only formulated from relatively small ions with well defined hydration numbers. They may also be prepared from macromolecules, which dissolve in water to give multiply charged species known as polyelectrolytes. Cements which fall into this category are polycarboxylates. For example, the zinc (II) poly(acrylate) is formed when the neutralization reaction of zinc (II) oxide takes place in an aqueous solution of poly (acrylic acid).

Polyelectrolytes form the basis of those cements, which are distinguished by their ability to adhere to reactive surfaces. Nowadays, the main use of such cements lies in the medical field, principally in dental surgery. They adhere permanently to biological surfaces where they must withstand adverse conditions of wetness, chemical attack, the stress of biological activity and chemical and biological changes within the substrate. Nevertheless, adhesive bonds are maintained.

Polyelectrolytes are polymers having a multiplicity of ionizable groups. In solution, they dissociate into polyions and small ions of the opposite charge, known as counterions. One typical polyelectrolyte is the poly(acrylic acid). The shape or configuration of a polyion is known as its conformation. There are many possible conformations available to a polyion because of the flexibility of the main chain due to the free rotation of bonds. There are two broad kinds of polyion conformation: the random coil and the ordered helix. Random coil conformations can range from spherical contracted state to the fully extended cylindrical or rod-like form. The conformation adopted depends on the charge on the polyion and the effect of the counterions. When the charge is low the conformation is a contracted random coil. As the charge increases the chain extends under the influence of mutually repulsive forces to a rod-like form. Thus, when a weak polyelectrolyte acid is neutralized, its conformation changes from a compact random coil to an extended chain. Poly(acrylic acid) shows this behaviour [8].

As mentioned before poly(acrylic acid) and its salts have been known to have useful binding properties for some years; they have used for soil consolidation [1], [2], [11-13,[16], [19], [22], [23], [25], [27-32] and as flocculant [24].

The most common poly(alkenoic acid) used in polycarboxylate cements is poly(acrylic acid), PAA. These poly(acids) are prepared by free-radical polymerization in aqueous solution using ammonium persulfate as the initiator and isopropyl alcohol as the chain transfer agent [5]. Under these conditions, the molecular weight of the PAA obtained lies below 10,000.

The cement-forming reaction of the polyelectrolyte cements may be considered to take place in a number of overlapping stages. These are the attack by the acid on the base, the migration of the liberated ions from the base in the aqueous phase, the ionization of the poly(acid) with consequent unwinding of the polymer chain, the interaction between the charged chains and cations leading to ion binding and gelation, and the hardening phase [3].

The molecular structure of the polyelectrolyte cements has been examined by a number of workers [19], [22], [29], [30], [32] using infrared spectroscopy. Empirical correlations between the carbon-oxygen stretching frequencies of the carboxylate ions and the nature of their coordination have been used [9], [20]. They basically consider the difference between the asymmetric and symmetric stretching frequencies, of the carboxylate group, to discern among different possible structures. A carboxylate ion can coordinate to metals in three ways: monodentate ligand, bidentate chelating ligand and bidentate bridging:

Ionic metal carboxylates are also possible, but in these compounds the cations are constrained to remain in the vecinity of the carboxylates anion by a general electrostatic field and there are no specific binding sites. Sodium poly(acrylate) is an example of ionic carboxylate.

Infrared spectroscopy offers a useful means of studying interactions betwen cations and carboxylate groups in liquids, solids and gels. Vibrations due to the carboxylic acid, -COOH, (~1700 cm^{-1}) can be distinguished from those of the carboxylates ion, $-COO^{-1}$, and are affected by hydrogen bonding. The C-O stretching vibrations of the carboxylate ion are influenced by the action. The asymetric mode is more sensitive than symetric mode. These frequencies vary from 1650 to 1500 cm^{-1}.

The goal of this study is to show the reaction of metal oxide and metal halide with poly(acrylic acid) by infrared spectroscopy. Also we propose a possible structure of cobaltic salt of the PAA, using empirical correlations between the carbon-oxygen stretching frequencies of the carboxylate ions and the nature of their coordination.

2. Experimental procedure

2.1. Materials

Solutions of aqueous poly(acrylic acid), 30% w/w, were prepared by polymerizing acrylic acid using the procedure of solution polymerization [5]. The PAA (8,000 g/mol average viscosimetric molecular weight) was prepared using as initiator ammonium persulfate and a chain-transfer agent 2-propanol. The initiation was carried out by means of free radicals who were obtained from the descomposition of ammonium persulfate. The dispersion was thermodynamically unstable and needed continuous agitation to prevent the coalescence and to dissipate the reaction heat. The polymerization required nitrogen to displace the oxygen which acts as inhibitor of the reaction. Polymerization was carried at 70 1°C in a stainless steel Parr Reactor of 300 mL with stirrer, control temperature and with nitrogen purge. The identification of the PAA was made by infrared spectroscopy. The polymers were neither fractioned nor purified.

Commercial Cobalt(III) Oxide (Co_2O_3) was employed in this study. This is a black power (95% Co_2O_3 and 5% CoO) from Union Miniere of Belgium. Co_3O_4 is your real chemistry formula; your name is tricobalt tetraoxide and your molecular weight: 241 g/mol.

Commercially available Cobalt Trifluoride (CoF_3) was employed in this study. This is a light-brown power from Aldrich Chem. Co. It discolors rapidly on exposure to moist air. Molecular weight: 116 g/mol.

2.2. Sample preparation

Cobalt (III) poly (acrylate) was prepared by mixing PAA solution and metal oxide power or metal halide power and manually stirring the mixture for one minute on a glass block using a dental spatula. Pastes were prepared at 18°C. A viscous black paste was obtained with cobalt (III) oxide. A viscous light yelow paste was obtained from the reaction with cobalt trifluoride. The material was submitted for analysis to determine the microstructure. All pastes were transferred to an AgCl crystal which was placed in the spectrometer as quickly as possible. The infrared measurements were taken using a Nicolet 510P spectrometer with a Nicplan IR-Microscope. Spectra were recorded a different times with 32 scans.
The number of moles of acrylic acid monomer units in PAA ware calculated, molecular weight: 72 g/mol. Different number of moles of Co_3O_4 and CoF_3 were used.
The characterization of cobalt (III) poly(acrylate) was performed by comparing the FTIR spectra of unreacted PAA with samples of polysalts of cobaltus prepared as was explained above. The spectra were recorded between 4,000 and 400 cm^{-1}. Band assignments are based on the standard texts by Nakamoto [20], Nyquist [26], and Bellamy [21]. Bands of particular importance to the present study were the carbonyl C=O stretching mode of the carboxylic acid group and the asymmetric and symmetric carboxylic COO^{-1} stretching modes of the carboxylate groups.

3. Results and discussion

3.1. Preparation of samples using Co3O4

The reaction between PAA and Co_2O_3 and CoO, considering PAA as the number of moles of acrylic acid monomer units in the polymer which is (-CH_2=CH(COOH)-), is:

$$8\ PAA + Co_2O_3 + CoO \sim 2\ CoPA^{III} + CoPA^{II} + 4\ H_2O$$

In fact the reaction shows two consecutive reactions. One yields cobalt(II) poly(acrylate) and other yields cobalt(III) poly(acrylate):

$$2\ PAA + CoO \sim CoPA^{II} + H_2O$$

$$6\ PAA + Co_2O_3 \sim 2\ CoPA^{III} + 3\ H_2O$$

Figure 1 shows the Fourier transform infrared spectra of unreacted PAA and cobalt (III) poly (acrylate) -COPA-. The spectrum of unreacted PAA displayed bands at ~3400 cm^{-1} (H_2O, reaction is in aqueous solution), ~1700 cm^{-1} (characteristic stretching, COO^{-1}, this is marked with number 1), ~1450 cm^{-1} and ~1400 cm^{-1} (scissors and bending vibrations of CH_2 and CHCO) and ~1230 cm^{-1} (OH bending of neighboring carboxyl group). The spectra of COPA exhibited bands at ~1550 cm^{-1} (asymmetric COO^{-1} stretching, this is marked with number 2; the peak at 60 s is more short that the peak at 3240 s), ~1400 cm^{-1} (symmetric COO^{-1} stretching, this is marked with number 2). The characteristic stretching band of the carbonyl group shifted from ~1700 cm^{-1} to ~1550 cm^{-1}. The peaks in ~1230 cm^{-1} in the unreacted PAA decreased in both spectra. These data indicates that cobalt (III) poly (acrylate) was present in the material.

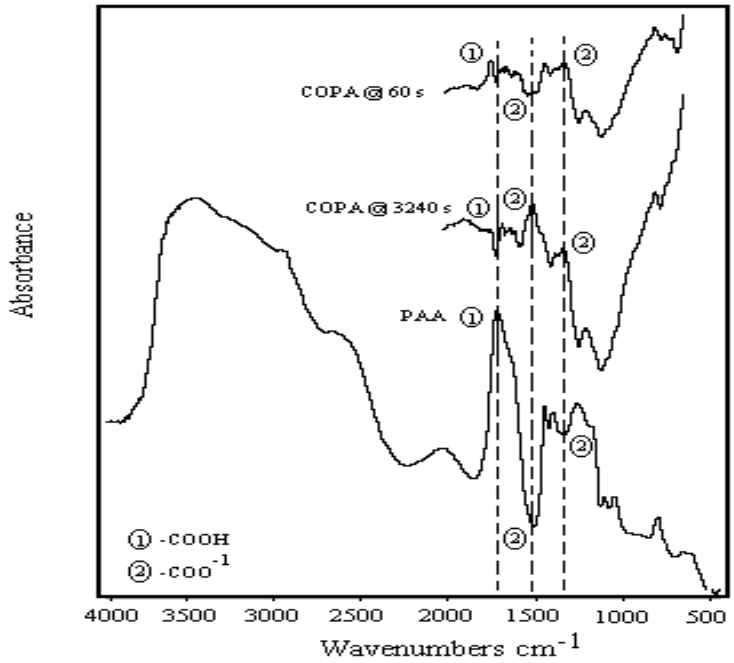

Fig. 1: Ftir Spectrum of Poly (Acrylic Acid) and Cobalt (Iii) Poly (Acrylate) Using 0.00498 Mol of Co_3o_4 and 0.0151 Mol of Paa or Paa/Co_3o_4 = 3.

Figures 2, 3 and 4 show the FTIR spectra of unreacted PAA and cobalt (III) poly (acrylate) salts with different molar ratios of PAA and Co_3O_4.

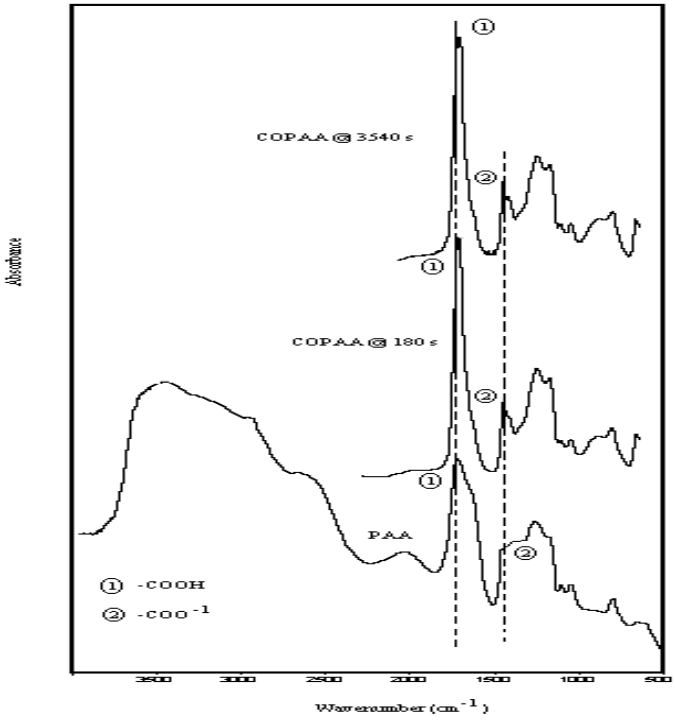

Fig. 2: Ftir Spectrum of Poly (Acrylic Acid) and Cobalt (Iii) Poly (Acrylate) Using 0.00415 Mol of Co_3o_4 and 0.00123 Mol of Paa or Paa/Co_3o_4 = 0.3.

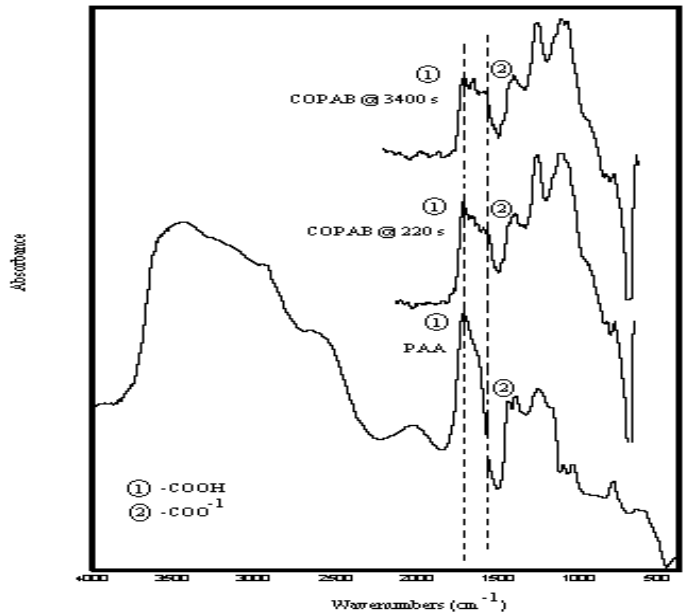

Fig. 3: Ftir Spectrum of Poly (Acrylic Acid) and Cobalt (Iii) Poly (Acrylate) Using 0.1390 Mol of Co_3o_4 and 0.00207 Mol of Paa or Paa/Co_3o_4 = 0.015.

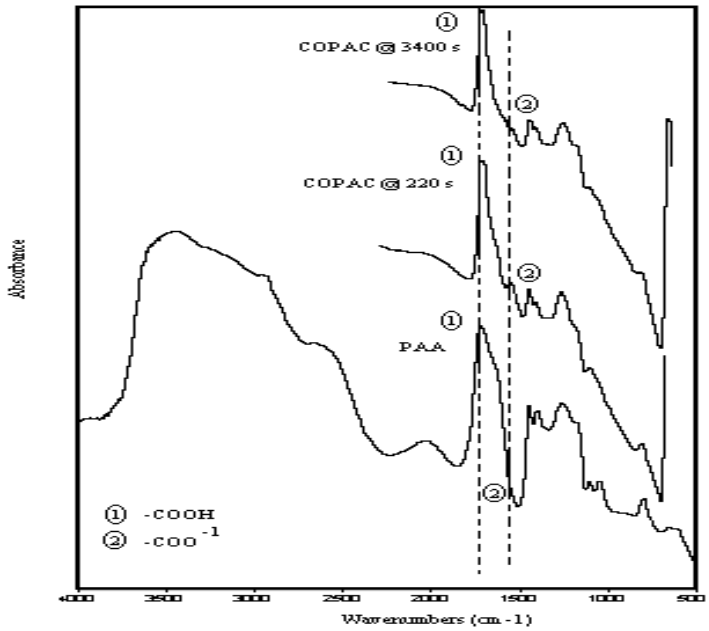

Fig. 4: Ftir Spectrum of Poly (Acrylic Acid) and Cobalt (Iii) Poly (Acrylate) Using 0.3930 Mol of Co_3o_4 and 0.01130 Mol of Paa or Paa/Co_3o_4 = 0.030.

The general pattern of behavior observed in the reacting pastes of PAA with Co (III) compounds was for the C=O stetching band (at 1700 cm^{-1}) of the carboxylic acid group to decline coincidently with the appearance and ehhancement of the COO^{-1} stretching bands of the metal carboxylates observed in the asymmetric stretch regions and the symmetric stretch regions. These results are indicative of an acid-base reaction.

3.2. Preparation of samples using CoF3

The reaction between PAA and CoF_3, considering PAA as the number of moles of acrylic acid monomer units in the polymer which is (-CH_2=CH(COOH)-), is:

$$PAA + CoF_3 \sim CoPA^{III} + HF.$$

As a matter of fact cobalt trifluoride reacts with water of PAA: [4], [14]

$$CoF_3 + 3H_2O \sim Co(OH)_3 + HF$$

According with the process, the second reaction is:

$$3\ PAA + Co(OH)_3 \sim CoPA^{III} + 3\ H_2O$$

Figure 5 shows the Fourier transform infrared spectra of unreacted PAA, unreacted CoF_3 and cobalt (III) poly(acrylate) -COPAD-. The spectrum of unreacted PAA displayed bands at ~3400 cm^{-1} (H_2O, reaction is in aqueous solution), ~1700 cm^{-1} (characteristic stretching, COO^{-1}, this is marked with number 1), ~1450 cm^{-1} and ~1400 cm^{-1} (scissors and bending vibrations of CH_2 and CHCO) and ~1230 cm^{-1} (OH bending of neighboring carboxyl group). The spectrum of unreacted CoF_3 displayed bands at ~740 cm^{-1} and weak shoulder ~860 cm^{-1} (this IR spectrum laboratory agrees with IR spectrum literature [26]).The spectra of COPAD exhibited bands at ~1470 cm^{-1} (asymmetric COO^{-1} stretching, this is marked with number 2; the peak at 150 s is more short that the peak at 3905 s), weak shoulder ~1400 cm^{-1} (symmetric COO^{-1} stretching), the weak shoulder at ~860 cm^{-1} became a real peak as the reaction continued. The characteristic stretching band of the carbonyl group shifted from ~1700 cm^{-1} to ~1470 cm^{-1}. The peaks in ~1230 cm^{-1} in the unreacted PAA decreased in both spectra. This occurrence indicates that cobalt (III) poly (acrylate) was present in the material.

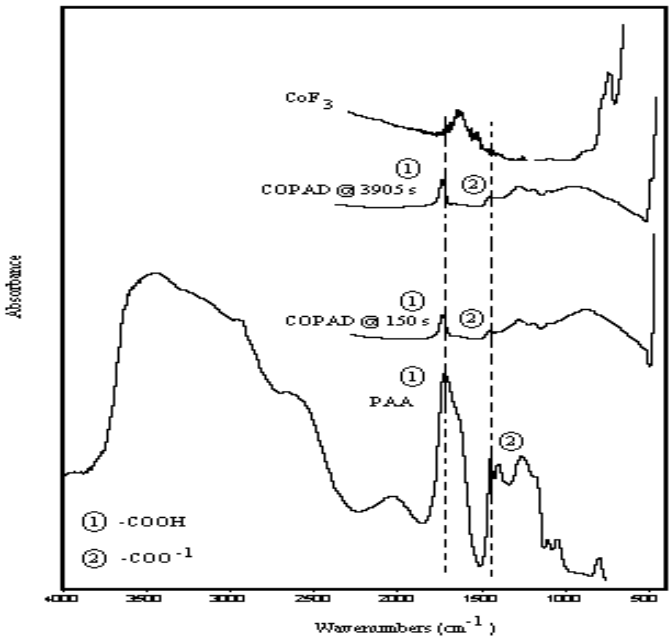

Fig. 5: Ftir Spectrum of Poly (Acrylic Acid) and Cobalt (Iii) Poly (Acrylate) Using 0.602 ~Mol of Cof_3 and 0.0215 ~Mol of Paa or Paa/Cof_3 = 0.036.

Figures 6, and 7 show the FTIR spectra of unreacted PAA and cobalt(III) poly(acrylate) salts with different molar ratios of PAA and CoF_3.

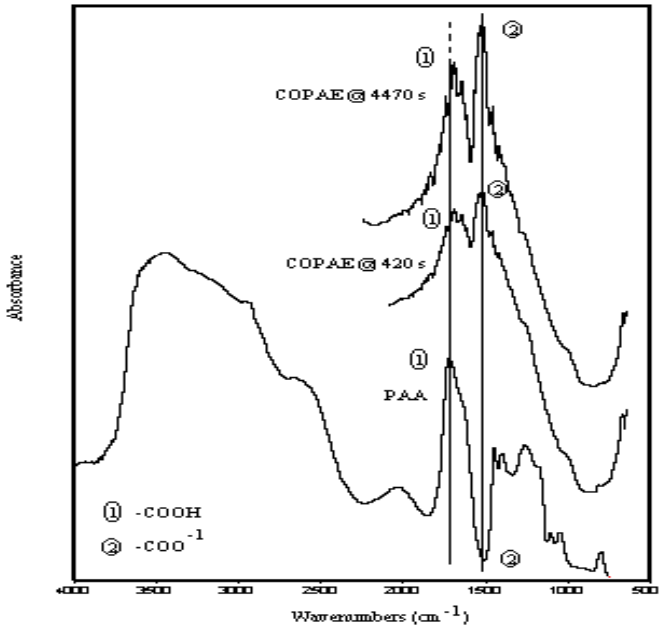

Fig. 6: Ftir Spectrum of Poly (Acrylic Acid) and Cobalt (Iii) Poly (Acrylate) Using 3.790 ~Mol of Cof_3 and 0.0328 ~Mol of Paa or Paa/Cof_3 = 0.009.

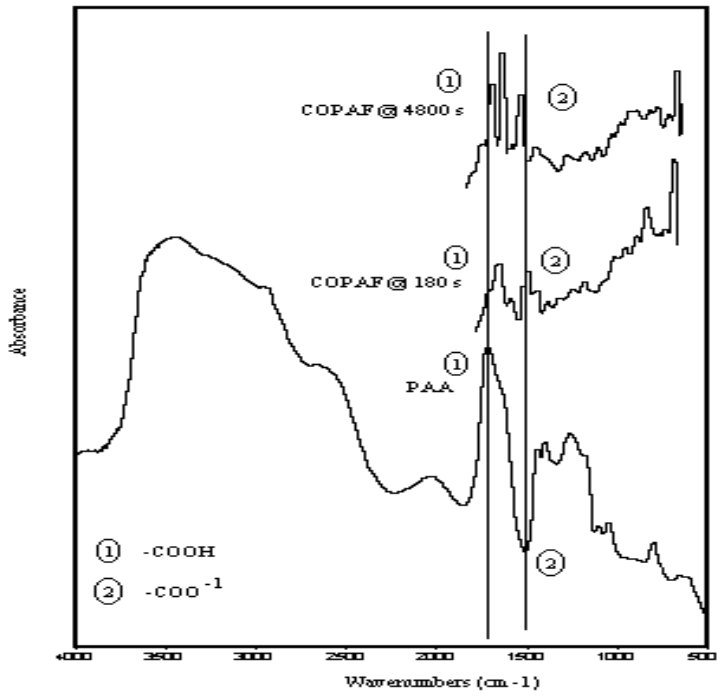

Fig. 7: Ftir Spectrum of Poly (Acrylic Acid) and Cobalt (Iii) Poly (Acrylate) Using 1.660 ~Mol of Cof_3 and 0.0238 ~Mol of Paa or Paa/Cof_3 = 0.014.

The general pattern of behaviour observed in the reacting pastes of PAA with Co(III) compounds was for the C=O stetching band (at 1700 cm^{-1}) of the carboxylic acid group to decline coincidently with the apparence and ehhancement of the COO^{-1} stretching bands of the metal carboxylates observed in the asymmetric stretch regions and the symmetric stretch regions. These results are indicative of an acid-base reaction.

The exact position of the asymmetrical and symmetrical COO^{-1} stretching modes can be used to obtain structural information. If the metal-carboxylate band is not ionic coordination complex are formed. There are bands with some covalent character then frequency shifts are to be expected. These shifts will depend on the metal-oxygen interaction and the nature of the coordination of the metal. Nakamoto [20] has suggested that there are four types of metal carboxylate structures: monodentate, bidentate bridging, bidentate chelating and ionic. It is possible to predict which structure is formed by knowing the wavenumber of the asymmetric and symmetric stretching vibrations. First, we

define $\Delta\nu=\nu_{as}-\nu_{s}$ where ν_{as} is the wavenumber of the asymmetric stretching and ν_{s} is the wavenumber of the symmetric stretching.

When sodium poly(acrylate) is formed the carboxylate group is ionically bonded. The band of the carbonyl group at ~1700 cm^{-1} is split in two new bands due to the asymmetric (~1500 cm^{-1}) and symmetric (~1400 cm^{-1}) stretching vibrations of the carboxylate anion formed. In this study, we found that the bands of the asymmetric and symmetric stretching to have frequencies of 1569 cm^{-1} and 1408 cm^{-1} respectively with a difference of 161 cm^{-1} [4].

All cobalt salts have $\Delta\nu$ between 105 and 200. Therefore, bidentate bridging structure may be tentatively assigned to cobalt(III) poly(acrylate). No matter which base is used (Co_3O_4 or CoF_3). However, there is a considerable proportion of unreacted PAA present in these reaction mixtures and free OH groups may play a role in the complex formation. Buckingham [6] stablishes the coordination number for cobalt(III) which is 6. This coordination number agrees with octahedrical stereochemistry structure. Therefore, octahedrical structure may be tentatively assigned to cobalt(III) poly(acrylate). Figure 8 shows schematically the proposed chemical structure of the hybrid formed [7], [10], [17], [18].

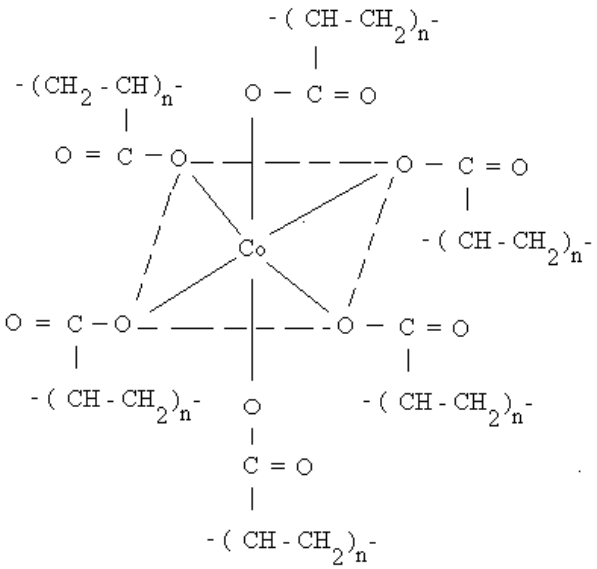

Fig. 8: Structure Propossed by Cobalt (Iii) Poly (Acrylate)

4. Conclusions

The oxide of the trivalent metal Co and the halide of the trivalent metal Co, react with aqueous solution of poly (acrylic acid) to form cobalt (III) poly (acrylate) a carboxylate salt. The halide of cobalt reacts with water of PAA first, then cobalt (III) hidroxide reacts with PAA to form the carboxylate salt. The structure could be a bidentate bridging. The coordination number for cobalt (III) is 6, and it agrees with octahedrical stereochemistry structure; therefore, octahedrical structure may be tentatively assigned to cobalt (III) poly (acrylate).

References

[1] A.D. Wilson, S. Crisp; "Organolithic Macromolecular Materials", Chapter 5, Applied Science Publishers, London, 1977.
[2] A. Padilla, J.L. Martinez, A. Sanchez, V.M. Casta-o; Mater. Lett, 12, 445 (1992) http://dx.doi.org/10.1016/0167-577X(92)90211-2.
[3] A. Wilson, J. Nicholson, "Acid-Base Cements", Cap. 5, Cambridge University Press, Cambridge U.K., 1993. http://dx.doi.org/10.1017/cbo9780511524813.
[4] B. Moody, "Comparative Inorganic Chemistry", 403-444, E. Arnold Division of Holder & Stoughton, Londres, 1991.
[5] C. Alvarez-Gayosso, J. Palacios-Alquisira, V. Casta-o; Intern. J. Polymeric Mater., in press.
[6] D.A. Buckingham, "Structure and Stereochemistry of Coordination Compounds", Inorganic Biochemistry, Cap. 1, Vol. I, G.L. Eichhorn Editor, Elsevier Scientific Publishing Company, Amsterdam, 1973.
[7] F. Hoffmann, M. Cornelius, J. Morell, M. Froda, Angewandte Chemie 45, 3216 (2006). http://dx.doi.org/10.1002/anie.200503075.
[8] F. Oosawa, "Polyelectrolytes", Marcel Dekker, New York, 1971.
[9] G.B. Deacon, R.J. Phillips, Coordination Chemistry Reviews, 33, 227 (1980) http://dx.doi.org/10.1016/S0010-8545(00)80455-5.
[10] G. Hernández, F. Rojas, M. García, M. Canseco,V.M. Casta-o, Mater. Sci. & Eng. A 355, 338 (2003) http://dx.doi.org/10.1016/S0921-5093(03)00101-1.
[11] H. Hu, J. Saniger, J. García-Alejandre, V. M. Casta-o, Mater. Lett. 12, 281 (1991) http://dx.doi.org/10.1016/0167-577X(91)90014-W.
[12] H. Hu, J. Saniger, V.M. Casta-o, Mater. Lett. 14, 83 (1992). http://dx.doi.org/10.1016/0167-577X(92)90179-N.
[13] H. Hu, J. Saniger, V.M. Casta-o, Mater. Lett. 16, 200 (1993). http://dx.doi.org/10.1016/0167-577X(93)90163-R.
[14] J. D. Lee, "Concise Inorganic Chemistry", Chapman & Hall, 783-799, New York, 1991.
[15] J. M. Saniger, H. Hu, V. M. Casta-o, J. García-Alejandre, Characterization Techniques for the Solid Solution Interface, 169-176.
[16] J. Saniger, H. Hu, V. M. Casta-o, Mater. Lett. 15, 113 (1992) http://dx.doi.org/10.1016/0167-577X(92)90024-E.

[17] J. Sun, S. Dong, E. Wang, J. Amer. Chem. Soc. 127, 13102 (2005) http://dx.doi.org/10.1021/ja0534809.
[18] J. Varela, V. Rodríguez, E. Rubio y V.M. Casta-o, J. New Mater. For Electrochem. Syst. 14, 59 (2011)
[19] J.W. Nicholson, S.J. Hawkins, E.A. Wasson; J. Mat. Sci., 4, 32 (1993)
[20] K: Nakamoto, "IR and RS of Inorganic and Coordination Compounds", Cap. 4, John Wiley & Sons, New York, 1986.
[21] L. J. Bellamy "The Infra-red Spectra of Complex Molecules",Methuen, London, 1954.
[22] M.A. Moharram, N. Abdel-Hakeem, H. Shaheen, R.M. Ibrahim, J. Mater. Sci., 21, 1986, 1681-1698. http://dx.doi.org/10.1007/BF01114725.
[23] M. Nicho, J. Saniger, M. Ponce, A. Huanosta, V. Casta-o, J. Appl. Polym. Sci., 66:861 (1977). http://dx.doi.org/10.1002/(SICI)1097-4628(19971031)66:5<861::AID-APP6>3.0.CO;2-T.
[24] N.T. Woodberry; Tappi, 44, 1961, 156A-160A.
[25] R.G. Hill, S.A. Labok; J. Mat. Sci., 26, 67 (1991) http://dx.doi.org/10.1007/BF00576034.
[26] R. Nyquist, R.O. Kagel, "Infrared Spectra of Inorganic Compounds", Academic Press, New York, 1971. http://dx.doi.org/10.1016/b978-0-12-523450-4.50005-5.
[27] R.P. Hopkins; Industrial & Engineering Chemistry, 47, 1955, 2258-2265. http://dx.doi.org/10.1021/ie50551a024.
[28] S. Crisp, B.E. Kent, B.G. Lewis, A.J. Ferner, A.D. Wilson, J. Dent. Res., 59, (6), 1980, 1055-1063. http://dx.doi.org/10.1177/00220345800590060801.
[29] S. Crip, H.J. Prosser, A.D. Wilson, J. Mater. Sci., 11, 36 (1976). http://dx.doi.org/10.1007/BF00541072.
[30] S.M. Rabie, A. Sawaby, M.A. Moharram, A.M. Nassar, K.H. Tahon, J. Appl. Polym. Sci., 41, 445, 1990. http://dx.doi.org/10.1002/app.1990.070410301.
[31] T.W. Lambe, A.S. Michaels; Chemmical Engineering News, 32, 1954, 488-492. http://dx.doi.org/10.1021/cen-v032n006.p488.
[32] W. Ho-Shing, J. Heay-Chain, H. Jiann-Wen, J. Appl. Polym. Sci., 63, 1997, 89-101. http://dx.doi.org/10.1002/(SICI)1097-4628(19970103)63:1<89::AID-APP9>3.0.CO;2-O.