

Application of Fourier Transform Infrared Spectroscopy To Study the Interactions of Poly(acrylic acid) and Mixtures of Poly(acrylic acid) and Polyacrylamide with Bone Powders and Hydroxyapatites

M. A. Moharram, Mousa A. Allam

Spectroscopy Department, Physics Division, National Research Centre, Doki, Cairo, Egypt

Received 11 October 2006; accepted 14 March 2007

DOI 10.1002/app.26581

Published online 24 May 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Fourier transform infrared (FTIR) spectroscopy was used to study the interactions of aqueous solutions of poly(acrylic acid) (PAA) and mixtures of aqueous solutions of PAA and polyacrylamide (PAAm) with chemically and thermally treated bone powders (BPs) and two commercial hydroxyapatites (HAs). An analysis of the spectra of the precipitates that resulted from the mixtures of PAA and the chemically treated samples of BP revealed that the spectra exhibited three new bands at 1544, 1552, and 1661 cm^{-1} . The first band was attributed to the formation of calcium–polycarboxylate resulting from the interaction between the carboxylic acid groups of PAA and the calcium ions of BP. The appearance of the other two bands, in addition to the disappearance of the band corresponding to the absorption of the acid groups of PAA, provided strong evidence for the exist-

tence of other interactions between the carboxylic acid groups and the amide groups of the organic matrix of BP. On the other hand, the FTIR spectra of the samples that resulted from the mixture of PAA and thermally treated BP and the two commercial HAs showed only a new absorption band at 1544 cm^{-1} . The interactions of mixtures of the aqueous solutions of PAA and PAAm, adjusted at low or high pH values, with the different BPs and HAs were examined. The mixtures of the aqueous solutions of PAA and PAAm interacted with the different BPs and two HAs, resulting in the formation of ternary PAA–BP–PAAm and PAA–HA–PAAm complexes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3228–3234, 2007

Key words: FT-IR; PAA; PAAm; HA

INTRODUCTION

Over the last 2 decades, extensive studies have been devoted to the interactions of water-soluble synthetic polymers such as poly(acrylic acid) (PAA) and polyacrylamide (PAAm) with metal salts, hydroxyapatites (HAs), and bones.^{1–13} Also, IR spectroscopy techniques have been used in the structural characterization of bones, HAs, and the compounds resulting from their interactions with water-soluble synthetic polymers.^{14–21}

An HA [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] implant of biological origin was also prepared.⁷ The natural apatite, prepared from compact bone, was compared with synthetic hydroxyapatite (SHA). *In vitro* and *in vivo* studies showed that the natural apatite was well tolerated and had better osteoconductive properties than SHA.

The formation of synthetic analogues of bones and teeth is a continuing objective. Bones and teeth are

microstructurally and compositionally complex, containing both organic and inorganic constituents.

It has been accepted that synthetic polymers make up the most diverse class of biomaterials because they offer a broad range of advantages over metals, glasses, and ceramics. Among these advantages are their low densities, chemical inertness, flexibility, elasticity or rigidity according to the need, and ease of fabrication into intricate shapes.⁶

Water-soluble polymers, such as PAA and PAAm, constitute a very important class of these synthetic polymers. Within the wide range of applications of synthetic polymers as biomaterials are their uses as substitutes or parts of organs, such as heart valves, blood vessel replacement tubes, bone replacements or sockets, bone cement, replacement corneas, and permanently implanted artificial teeth. Also, some synthetic polymers such as poly(vinyl pyrrolidone) have been used as plasma expanders. A very important application is the use of synthetic polymer membranes for hemodialysis and water purification.⁶

Accordingly, this study was aimed at the application of Fourier transform infrared (FTIR) spectroscopy to the investigation of the materials resulting from the interactions of PAA and mixtures of PAA and PAAm with bone powders (BPs) and HAs.

Correspondence to: M. A. Moharram (moharram1937@yahoo.com).

EXPERIMENTAL

In this study, BP was prepared from freshly removed diaphyses of long calf bones. The bones were dissected from surrounding connective tissues and alkali-treated to leave purely osseous structures free of all traces of tissues, fats, or any organic matter occupying the intraosseous spaces. In the alkali treatment, the bones were broken into small pieces and boiled for hours in a 30% sodium carbonate solution; this was followed by thorough washing with hot water. The treated bones were then dried at 100°C overnight. The cycle of the alkali treatment was repeated until a constant weight for the sample was reached. Then, the bones were ground into fine powders in a hardened steel vial. The BP was sieved to obtain a suitable size (90–125 μm) for FTIR measurements.

The chemically treated BP samples were then heated in a conventional oven at 700°C for 2 h.

PAAm was obtained from BDH Chemicals (Pool, England); its molecular weight was over 5,000,000. PAA was obtained from Nisso Shoji Co. (Tokyo, Japan; PW-110, lot no. 4029) with a molecular weight of 125,000. The two polymers were used without any further purification. A solution of each polymer was prepared by the dissolution of 1 g in 100 mL of distilled water. Each solution was then stirred overnight to ensure complete dissolution. The chemically treated BP was added to the 1% aqueous solution of PAA with different concentrations (wt %). Then, the mixtures were stirred with a magnetic stirrer at room temperature for 2 h without any pH adjustment. The precipitate was filtered and washed with distilled water to remove any soluble salts. The samples were dried in an oven at 90°C for 6 h and then ground to a particle size suitable for IR measurements. The FTIR measurements were carried out with a single-beam FTIR spectrophotometer (FT/IR-430, Jasco, Tokyo, Japan).

RESULTS AND DISCUSSION

The FTIR spectra of both chemically and thermally treated BPs are shown in Figure 1(a,b), respectively. The spectra of the chemically treated samples exhibit, in addition to the characteristic absorption bands of the phosphate ions (PO_4^{3-}) at 563, 603, 960, and 1032 cm^{-1} and the characteristic absorption bands of carbonate ions (CO_3^{2-}) at 870, 1415, and 1467 cm^{-1} , another medium-intensity band at 1655 cm^{-1} . The appearance of the 1655- cm^{-1} band indicates the presence of a residual trace of organic matter. This band is assigned to the C=O stretching vibration of amide I.

The chemically treated sample was then heated at 700°C for 2 h to remove the residual organic matter. It is apparent from Figure 1(b) that the band at 1655 cm^{-1} disappeared from the spectra of the heated

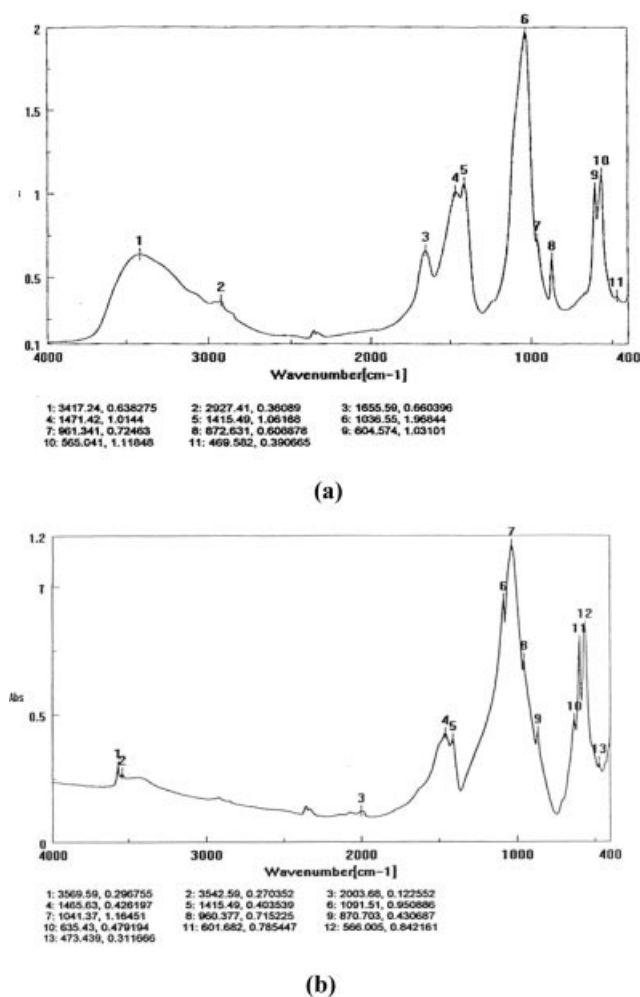


Figure 1 FTIR spectra of (a) chemically treated BP and (b) BP heat-treated at 700°C for 2 h.

sample; the spectrum is typical of the characteristic spectrum of carbonate-bearing HA.

For comparison, the FTIR spectra of both commercial bovine hydroxyapatite (BHA) and commercial SHA were recorded, and the spectrum of BHA is shown in Figure 2. This figure shows only the characteristic absorption bands of HA.

An aqueous solution of PAA (1 wt %) was prepared. Mixtures of this solution and chemically treated BP were prepared with different concentration ratios (wt %) with respect to each other. The precipitates were separated, dried, and ground into fine powders with a particle size of 90 μm . KBr discs from these powders were measured with FTIR spectroscopy. A careful examination of these spectra revealed that the addition of BP to PAA with different concentrations resulted in the following changes in the spectral features of each of PAA and BP (Fig. 3).

Over the OH and N—H stretching region from 3500 to 3100 cm^{-1} , the spectrum of PAA exhibits two peaks at 3392 and 3172 cm^{-1} , and the spectrum of BP [Fig. 1(a)] displays an absorption band at 3420 cm^{-1} ,

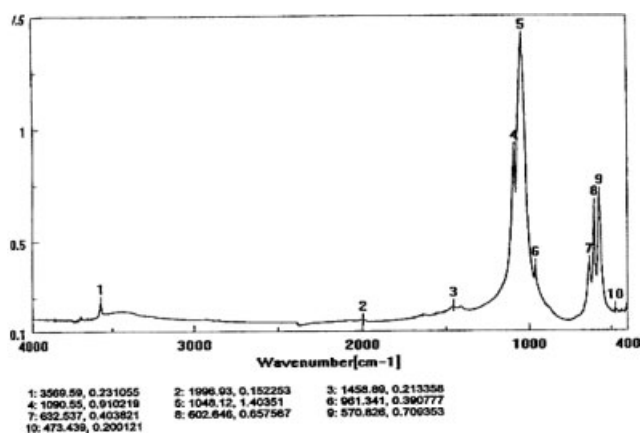


Figure 2 FTIR spectrum of commercial BHA.

whereas the spectrum of the precipitate that resulted from mixing 75% PAA and 25% BP shows a strong broad absorption band at 3447 cm^{-1} with a shoulder at about 3250 cm^{-1} . Increasing the concentration of BP to 50 and 75% resulted in the appearance of only a strong broad band at 3430 and 3401 cm^{-1} , respectively.

Mixing 75% PAA and 25% BP resulted in the appearance of a new absorption band at 1544 cm^{-1} and a shift in the position of the C=O stretching band of PAA from 1711 to 1718 cm^{-1} . This may refer to a chemical reaction between PAA and BP via polycarboxylate formation. Increasing the BP concentration to 50 and 75% resulted in the appearance of two new strong bands at about 1661 and 1552 cm^{-1} accompanied by the complete disappearance of C=O of PAA. This means that the acid is completely consumed in a considerable reaction with the residual organic matrix of BP.

On the basis of the foregoing considerations, it may be concluded that the new absorption band that appears at 1543 cm^{-1} in the spectrum of the sample containing 25% BP is likely due to the COO^- structures. This means that calcium of BP may be involved in the reaction with PAA forming calcium-polycarboxylate.

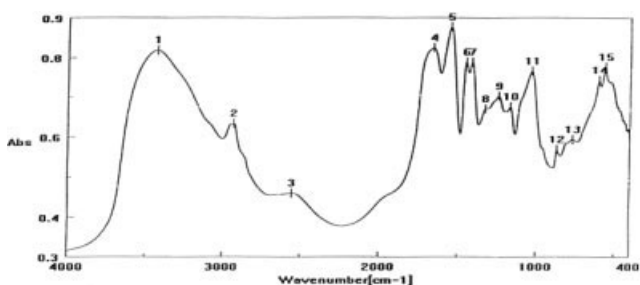


Figure 3 FTIR spectrum of the precipitate formed from a mixture of 50% PAA and 50% BP.

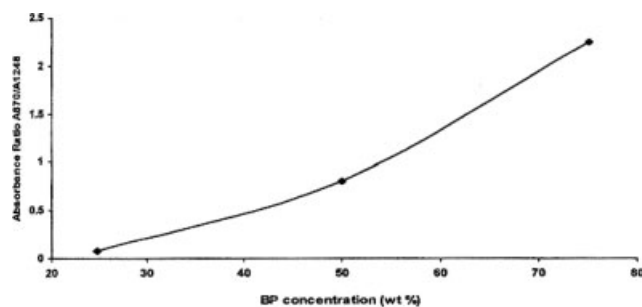


Figure 4 Variation of the absorbance ratio (A_{870}/A_{1246}) in the FTIR spectra of the resultant precipitates of mixtures of PAA and BP with the concentration of BP.

The appearance of two new strong bands at 1661 and 1552 cm^{-1} , together with the disappearance of C=O of PAA, in the spectra of samples containing 50 or 75% BP could be attributed to the complete utilization of the carboxylic groups (COOH) of the acid in another reaction between PAA and the amide groups of the organic matrix of BP. The nonlinear behavior of the relationship between the A_{870}/A_{1246} ($\text{cm}^{-1}/\text{cm}^{-1}$) ratio and the concentration of BP in the mixture (Fig. 4) gives more evidence for the presence of chemical reactions between PAA and BP.

The aqueous solution of PAA was also mixed with different concentrations (wt %) of thermally treated BP [i.e., heated bone powder (HBP)]. Homogeneous milky mixtures were formed without any precipitation. The mixtures were then cast onto plastic dishes and left to form dry, solid films. After drying, the films were ground into fine particles suitable for KBr discs. An example of FTIR spectra of the samples is shown in Figure 5.

An analysis of the spectra revealed that the addition of 25 wt % HBP to the PAA solution resulted in the appearance of a broad strong band at 3441 cm^{-1} with a weak shoulder at about 3255 cm^{-1} . The addition of 50 and 75 wt % HBP to the PAA solution resulted in the appearance of only one broad strong absorption band at 3440 and 3430 cm^{-1} , respectively.

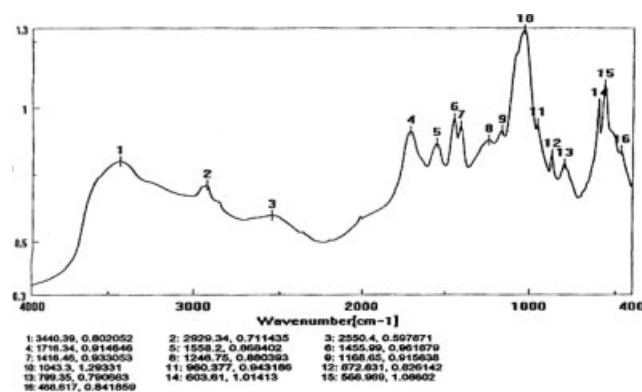


Figure 5 FTIR spectrum of the result of a mixture of 50% PAA and 50% HBP.

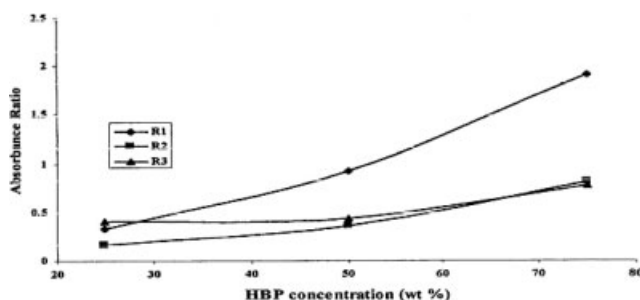


Figure 6 Variation of the absorbance ratios ($R_1 = A_{566}/A_{1711}$, $R_2 = A_{870}/A_{1711}$, and $R_3 = A_{1550}/A_{1711}$) with the concentration of HBP.

Also, for any given concentration of BP, the spectra of the powders that resulted from the mixtures exhibited a new absorption band of medium intensity at 1559–1555 cm^{-1} .

The observed changes in the spectral features of the absorption bands in the O–H stretching region together with the appearance of the band at 1559–1555 cm^{-1} indicate that a type of reaction took place between PAA and HBP.

The nonlinear relationship between the absorbances ratios [A_{586}/A_{1711} , A_{870}/A_{1711} , and A_{1550}/A_{1711} ($\text{cm}^{-1}/\text{cm}^{-1}$)] and the concentration of HBP in the solution (Fig. 6) provides more strong evidence for the presence of an interaction between PAA and HBP.

The interaction between the aqueous solution of PAA and each of the two commercial HAs was also investigated. This interaction was demonstrated first by the appearance of a strong broad band in the region of O–H stretching vibrations at 3435 cm^{-1} and a new absorption band at 1565 cm^{-1} (Fig. 7) in the case of the powder that resulted from the mixing of an aqueous solution of PAA and 75 wt % BHA and SHA and second by the nonlinear relationship between the concentration of the powder and each of the aforementioned absorbances ratios, as shown in

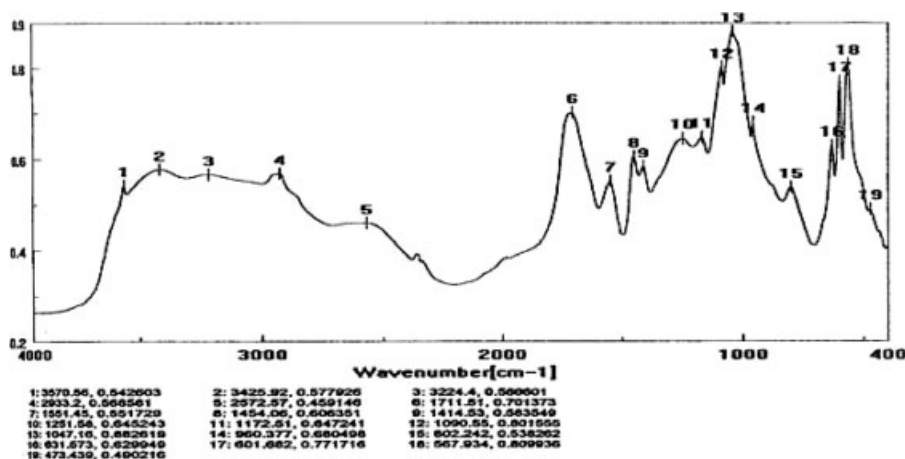


Figure 7 FTIR spectrum of the result of a mixture of 50% PAA and 50% BHA.

Figure 8. However, the extent of the interaction in the case of the two commercial HAs, for any given concentration of the powder, was always weaker than that in the case of HBP.

The aforementioned findings lead to the conclusion that the most striking changes that can be pointed out in these results are the change in the OH region, the appearance of the new band at 1555 cm^{-1} , and the significant decrease in the intensity of the absorption band of C=O groups of PAA. Therefore, it may be concluded that a reaction took place between the calcium content of HBP and the COOH groups of the PAA, forming calcium–polycarboxylate. This may explain the decrease in the intensity of C=O of PAA with an increasing HBP concentration and the appearance of the new band at 1559–1555 cm^{-1} , which can be attributed to the stretching vibration of COO^- . The increase in the absorbance ratio, $R_3 = A_{1550}/A_{1711}$, reflects the increase in the polycarboxylate formation as the HBP concentration increases.

Also, it is apparent from these spectra that a residual acid was still there, and this may be due to the fact that HBP has no amide that can take part in another reaction with this residual acid. This is more evidence for the reaction between the amide of the chemically treated BP and the residual acid in addition to the reaction of polycarboxylate formation. In the case of HBP, only the reaction of calcium–polycarboxylate formation occurred.

Each of the chemically and thermally treated BPs and the two commercial HAs were mixed with a mixture of 50 wt % PAA and 50 wt % PAAm in different concentrations without any pH adjustment. Thin films were then prepared from these mixtures. Examples of FTIR spectra of the films are shown in Figure 9(a,b). A visual examination of the spectra reveals that the addition of 10 wt % chemically treated BP to the mixture of PAA and PAAm resulted in the appearance of a new weak band at 1558 cm^{-1} and in

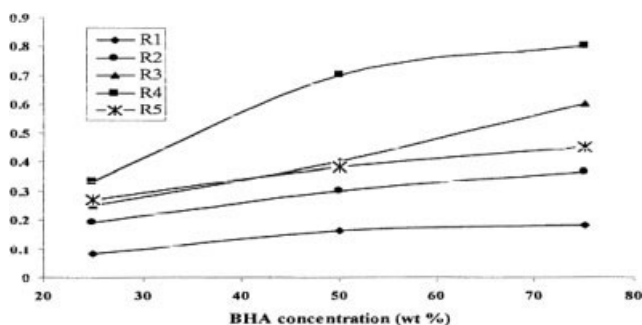


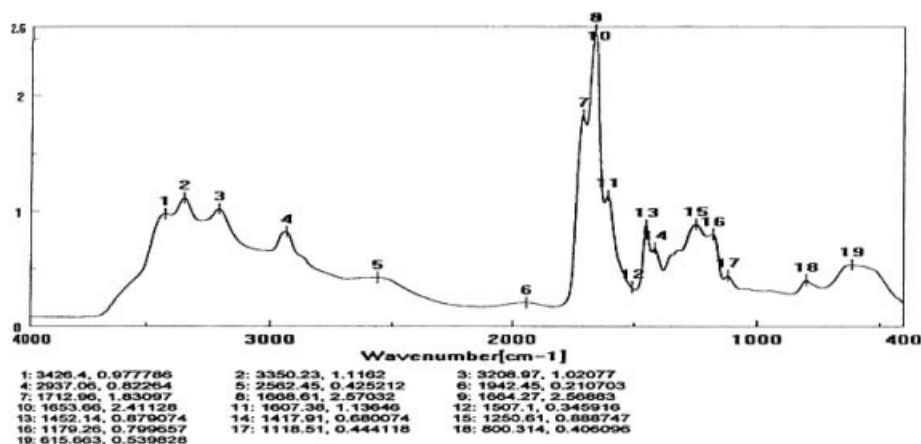
Figure 8 Variation of the absorbance ratios ($R_1 = A_{960}/A_{1711}$, $R_2 = A_{1090}/A_{1711}$, $R_3 = A_{960}/A_{1454}$, $R_4 = A_{1090}/A_{1454}$, and $R_5 = A_{1550}/A_{1711}$) in the FTIR spectra of the results of mixtures of PAA and BHA with the concentration of BHA.

a considerable decreases in the intensity of the C=O band of PAAM. Increasing the concentration of BP to 30, 50, and 70% resulted in a complete disappearance

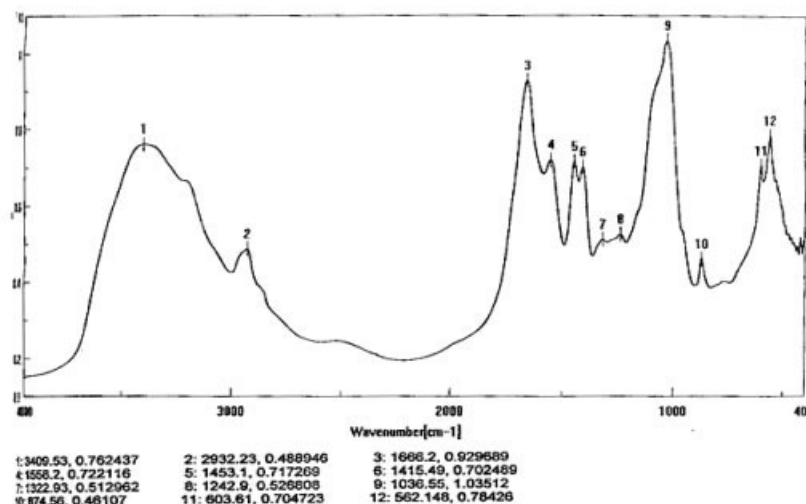
of the C=O band of PAA and in the appearance of two new bands in the spectral ranges of 1672–1666 and 1574–1556 cm^{-1} . The position of these two peaks depends on the concentration of BP. This result gives strong evidence that the carboxylic acid groups of PAA were consumed in reactions with the amide group of BP.

On the other hand, the appearance of the new band at 1558 cm^{-1} in the spectrum of the sample containing 10% BP may be attributed to the reaction between the calcium ions of BP and COOH of PAA, which resulted in the formation of the calcium–polycarboxylate complex.

An analysis of the spectra of the samples containing a mixture of 50 wt % PAA–PAAM and BHA with different concentrations showed that for any concentration of BHA (from 10 to 70 wt %), the spectra displayed a well-defined new shoulder in the spectral

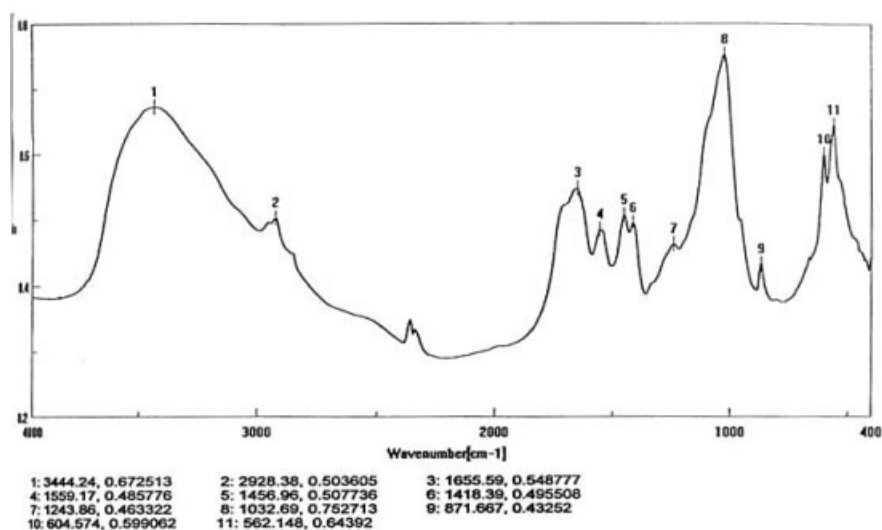


(a)

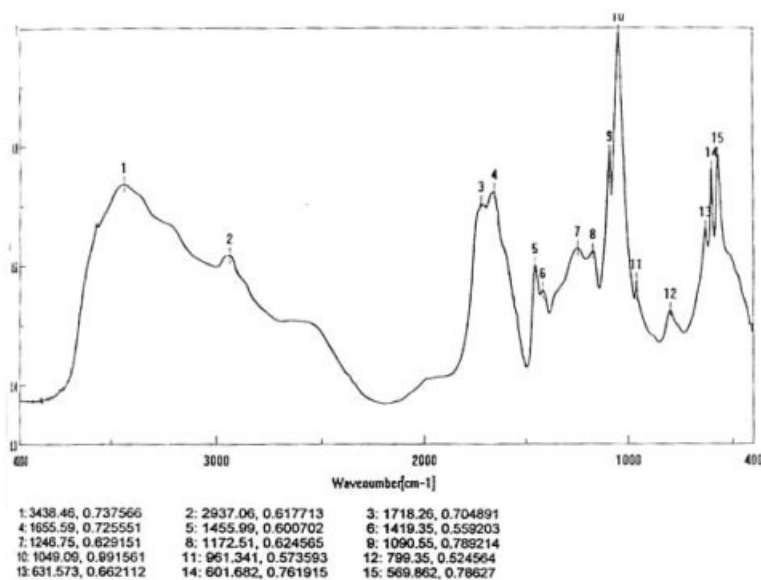


(b)

Figure 9 FTIR spectra of (a) a film of a mixture of 50% PAA and 50% PAAM and (b) the result of a mixture of 50% PAA–PAAM and 50% BP.



(a)



(b)

Figure 10 FTIR spectra of (a) a complex of 50% PAA-PAAm and 50% BP and (b) a complex of 50% PAA-PAAm and 50% BHA.

range of $1563\text{--}1556\text{ cm}^{-1}$. The spectrum of the sample containing 10 wt % BHA showed a weak shoulder at about 1705 cm^{-1} . The shoulder, which corresponds to the absorption of $\text{C}=\text{O}$ of PAA, disappears from the spectra of the samples containing the higher concentrations of BHA. This means that an interaction took place between the Ca ion of BHA and the carboxylic groups of PAA. However, the rate of the interaction in this case was weaker than rate of the interaction of BP and HBP carboxylic groups.

The pH value of the mixtures under investigation was adjusted to values promoting the formation of

precipitates. The formed precipitates were then dried and ground into a particle size suitable for preparing KBr discs required for FTIR measurements. Through a comparison of the FTIR spectra, the following induced changes are visible:

1. The spectra of the precipitate that resulted from the interaction of PAA with PAAm at a low pH value showed spectral features similar to those of the two polymer components of the mixtures, although the bands appeared at shifted positions and with different intensities. These differences

in the positions and intensities of the absorption bands were attributed to the formation of an interpolymer complex resulting from the interaction between PAA and PAAm solutions at a low pH, and hydrogen bonding was the mechanism of the interaction between the two polymers.

- The spectrum of the samples containing 50 [Fig. 10(a)] or 75 wt % BP exhibited a new absorption band at 1556 cm^{-1} . The appearance of this band was strong evidence for the formation of another interaction between the Ca ions of BP and the residual acid groups of PAA.
- The intensity of the absorption band at 1655 cm^{-1} belonging to the absorption ($\nu\text{C}=\text{O}$) band in the spectrum of the PAA–PAAm complex increased with increasing BP concentration, and its peak height was higher than that of the band at 1556 cm^{-1} . This may be due to the interaction of the acid group with the residual organic part in BP.

The A_{1718}/A_{870} ($\text{cm}^{-1}/\text{cm}^{-1}$) absorbance ratio was plotted against the concentration of BP in the mixture. This nonlinear relationship suggested the existence of an interaction of the amide group of the organic part in the band and the acid groups of the PAA bone.

A comparison of the spectra of the precipitates that resulted from the mixing of BP with PAA–PAAm mixtures with various concentration and those of the precipitates that resulted from the mixing of BHA with the same solution with different BHA concentrations [Fig. 10(b)] reveals that the most striking differences are as follows:

- The spectrum of the ternary PAA–BP–PAAm complex exhibits a weak band at 1558 cm^{-1} . This band appears as a very weak shoulder in the spectra of the ternary PAA–BHA–PAAm complex.
- There is no evidence for the presence of any interaction between the acid groups and BHA, particularly in the region of the $\nu\text{C}=\text{O}$ band of the PAA–PAAm mixture.

On the basis of the foregoing data, it could be concluded that a weak interaction took place between the Ca ions of HP and the residual acid group of PAA.

CONCLUSIONS

A careful examination of FTIR spectra of the samples under investigation demonstrated that the acid groups of PAA, a PAA–PAAm mixture, and a PAA–PAAm complex interacted with chemically treated BP via the Ca^{2+} ions and the amide groups of the residual organic part in the bone matrix. These acid groups interacted also with thermally treated BP and the two HAs via the Ca^{2+} ions only.

The rate of interaction of the acid groups with the calcium contents of HAs was always weaker than that in the case of thermally treated BP.

References

- Cooke, F. W. *Clin Orthop Relat Res* 1992, 27, 135.
- Fukuda, R.; Yoshida, Y.; Nakayama, Y.; Okazaki, M.; Inoue, S.; Sano, I.; Suzuki, K.; Shintani, H.; Van Meerbeek, B. *Enamel Dent Biomater* 2003, 24, 1861.
- Labella, R.; Braden, M.; Dep, S. *Biomaterials* 1994, 15, 1197.
- Misra, D. N. *J Colloid Interface Sci* 1996, 181, 289.
- Mun, G. A.; Nurkeeva, Z. S.; Khutoryanskig, V. V.; Sarybayeva, G. S.; Dubolazove, A. V. *Eur Polym J* 2003, 39, 1687.
- Park, J. B. *Biomaterials Science and Engineering*; Plenum: New York, 1984.
- Guizzard, S. *J Biomed Mater Res* 2000, 53, 227.
- Rabie, S. M.; Sawaby, A.; Moharram, M. A.; Nassar, A. M.; Tahon, K. I. *J Appl Polym Sci* 1990, 41, 445.
- Rey, C.; Miquel, J. L.; Facchini, L.; Legrand, A. P.; Glimcher, M. J. *Bone* 1995, 16, 583.
- Tsuchida, E.; Abe, K. *Adv Polym Sci* 1982, 45, 1.
- Wang, M. *Biomaterials* 2003, 24, 2133.
- Young, A. M.; Sherpa, A.; Pearson, G.; Schottlander, B.; Waters, D. N. *Biomaterials* 2000, 21, 1971.
- Zhang, S.; Gonsalves, K. E. *J Mater Sci: Mater Med* 1997, 8, 25.
- Dong, J.; Ozaki, Y.; Nakashima, K. *Macromolecules* 1997, 30, 1111.
- Moharram, M. A.; Ballomal, L. S.; El-Gendy, H. M. *J Appl Polym Sci* 1996, 59, 987.
- Moharram, M. A.; Higazy, H.; Khalil, S. *J Mater Sci* 1993, 28, 4010.
- Moharram, M. A.; Rabie, S. M.; El-Gendy, H. M. *J Appl Polym Sci* 2002, 85, 1619.
- Moharram, M. A.; El-Gendy, H. M. *J Appl Polym Sci* 2002, 85, 2699.
- Rehman, I.; Bonfield, W. *J Mater Sci: Mater Med* 1997, 8, 1.
- Rehman, I.; Smith, R.; Hench, L. L.; Bonfield, W. *Bioceramics* 1994, 7, 79.
- Weiss, P.; Lapkowski, M.; Legeros, R. Z.; Bouler, J. M.; Jean, A.; Daculsi, G. *J Mater Sci: Mater Med* 1997, 8, 621.