

X-Ray Photoelectron Spectroscopic Study of the Interaction between Polyacrylic Acid and Hydroxyapatite

Toshio NASU, Kunio NAGAOKA and Hideki AOKI*

Department of Technical Education, Faculty of Education, Yamagata University, Yamagata 990 Japan

**Institute for Medical and Dental Engineering, Tokyo Medical and Dental University Tokyo 101 Japan*

(Received September 1, 1988)

Abstract

Chemical interaction at the interface between hydroxyapatite plate and polyacrylic acid was studied by X-ray photoelectron spectroscopic method combined with Ar^+ ion beam etching technique to examine the mechanism of adhesion. It was confirmed that calcium in hydroxyapatite reacted with polyacrylic acid to form calcium polyacrylate.

1. Introduction

The phenomenon of the adhesion of dental polyelectrolyte cements is complex. Several processes occur simultaneously^(1,2) so that adhesive bond is composed of many attractive forces, two of these, electrostatic contribution and chemical contribution, which are important from the standpoint of the marginal seal and the endurance of bond joint. Carboxylate groups of polyacrylic acid (after this: PAA) seem to react with calcium in tooth enamel and the metal restoration, these reaction appears to be the basis of strong adhesive force of polyelectrolyte cement. D. C. Smith described the adhesion mechanism of dental cements which contain PAA^(3,4). PAA assumes to chelate with calcium in enamel. There have been several investigations on the chemical reaction between PAA and metal or metal oxide^(2,5,6,7,8). D. R. Beech showed that PAA reacts with calcium ions in enamel powder

in his infrared spectroscopic study⁽⁹⁾.

However, few experiments have been performed concerning the chemical interaction of tooth enamel with PAA at the intact bond joint. A technique is presented in which the chemical state of intact bond joint can be studied using x-ray photoelectron spectroscopy (ESCA). ESCA technique gives information of the chemical state on a solid surface to a 10-40 Å depth⁽¹⁰⁾. Different chemical states of an atom give chemical shifts in ESCA spectra⁽¹¹⁾. Chemical interaction of polyacrylic acid with metals was studied by ESCA method⁽¹²⁾. ESCA technique is suitable to perform the chemical state analysis of PAA-tooth enamel at adhesive bond joint. The hydroxyapatite is an essential part of tooth enamel. Therefore, the Ar^+ ion beam etching was applied to the hydroxyapatite plate coated with PAA to thin the PAA layer gradually in the sample chamber of ESCA equipment.

After a few minutes of etching, ESCA spectra were measured. Thus the chemical state of the calcium near the interface between PAA and hydroxyapatite was analyzed to examine the chemical constituent of the strong adhesive force of the cements.

2. Materials and methods

Preparation of specimens Hydroxyapatite powder was synthesized by hydrothermal reaction method and then sintered in the die under hydrostatic pressure of 2000 kg/cm at 1250°C⁽¹³⁾. Hydroxyapatite plate, thickness of 1 mm, diameter of 5 mm was cut from the sintered hydroxyapatite block. The physical characteristic of the sintered hydroxyapatite plate was as follows: sintering density was 99.9%, lattice constants a , c were 9.41 Å and 6.88 Å, density was 3.161 g/cm³. These hydroxyapatite plates were polished with No.600 emery paper, and then painted with a 2.5% by weight aqueous solution of PAA (Wako Pure Chemical Industries, Osaka), and dried in a desiccator for 24h. A human tooth enamel plate was prepared as standard for ESCA measurement to compare with the data of the hydroxyapatite plate.

Argon ion etching Ar⁺ ion etching was used to thin gradually the PAA film coated on the hydroxyapatite plate in the sample chamber of an ESCA spectrometer. A schematic illustration of argon ion etching is shown in Fig.1. High purity argon gas was led into the ionization chamber at about 5×10^{-5} mmHg. The argon ion beam was generated with a SHIMAZU Model ARE Sputter Ion Gun (Shimadzu Industries, Kyoto) which was operated with a beam potential of 1.5KV and electron emission current of 20mA.

ESCA measurement Experiments were performed in the SHIMADZU ESCA 650B Elec-

tron Spectrometer using Mg K α radiation (1253.5eV). The binding energies were corrected by using the values of 285.0eV of the C 1s level resulting from the contaminated carbon. After the argon ion beam etching for 1, 5, 10 and 15 min, the ESCA spectra of Ca 2p_{1/2} and 2p_{3/2} levels were measured respectively. The measurement was performed within the range of 340eV to 360eV at the scan rate of 0.2 eV/sec. Thus chemical interaction near the interface between PAA and the sintered hydroxyapatite plate was analyzed.

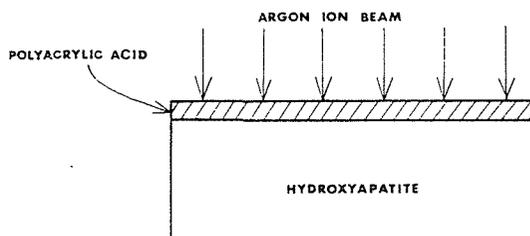


Figure 1. Schematic figure of argon ion etching of sintered hydroxyapatite plate coated with polyacrylic acid.

3. Result

Experimental ESCA spectra of a human tooth enamel and the sintered hydroxyapatite plate are illustrated in Fig.2. The abscissa shows binding energy of photoelectron released from the sample. The ordinate shows the intensity of the photoelectron in arbitrary unit. The profiles of sintered hydroxyapatite plate were almost the same as those of tooth enamel. Binding energy of electron in Ca 2p_{1/2} and Ca 2p_{3/2} orbitals of the sintered hydroxyapatite plate are 351.00 eV and 347.50 eV. Those of the tooth enamel are 350.90 eV and 347.55 eV, respectively. The ESCA spectra of the sintered hydroxyapatite plate coated with PAA are illustrated in Fig. 3. Binding energy of electron in Ca 2p_{1/2} and Ca 2p_{3/2} orbitals of the sintered hydroxyapa-

tite plate coated with PAA are 352.80 eV and 349.20 eV, shifted 1.8 eV and 1.7 eV to higher energy side compared with uncoated sample respectively. The profile of Ca $2p_{3/2}$ level on the Ar^+ ion etched sample for 1 min shows a peak at 349.50 eV and a shoulder at 347.50 eV. This shoulder appeared more clearly by the increasing of Ar^+ ion etching duration and grew a subpeak. Binding energy of this subpeak was almost the same as the Ca $2p_{3/2}$ orbital of uncoated sintered hydroxyapatite plate. The peak of Ca $2p_{1/2}$ level of sintered hydroxyapatite plate coated with PAA reduced in the height and became broader by increasing of the Ar^+ ion etching duration.

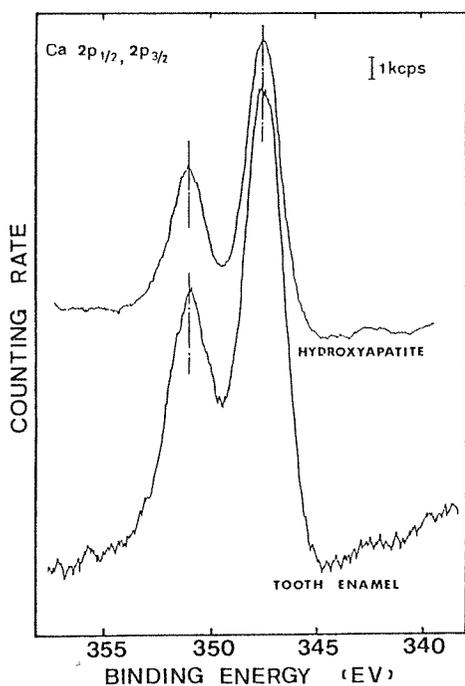


Figure 2. X-ray photoelectron spectra of Ca $2p_{1/2}$ and $2p_{3/2}$ levels of human tooth enamel and sintered hydroxyapatite plate.

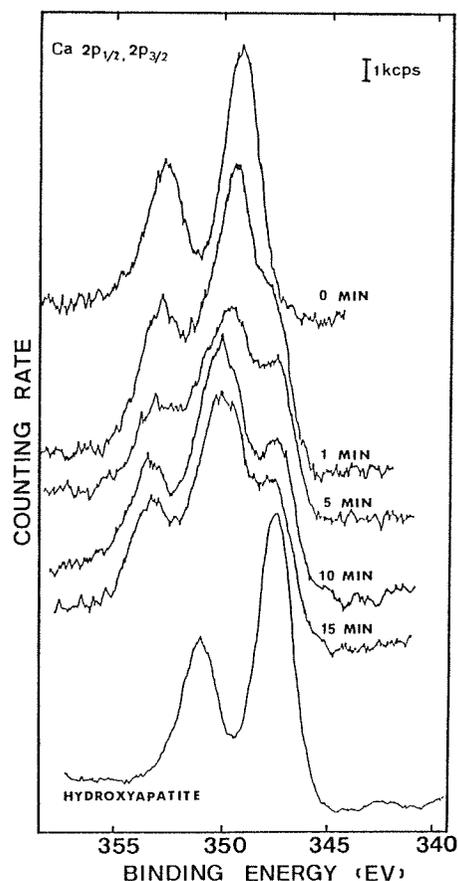


Figure 3. X-ray photoelectron spectra of Ca $2p_{1/2}$ and $2p_{3/2}$ levels of sintered hydroxyapatite plate coated with polyacrylic acid and etched by argon ion beam for 1, 5, 10 and 15 minutes and uncoated hydroxyapatite plate.

4. Discussion

Experimental ESCA spectra of the sintered hydroxyapatite plate coated with PAA showed that there are two chemical states of calcium near the interface. A chemical state corresponding to the subpeak which appeared in Ca $2p_{3/2}$ orbital of the Ar^+ ion etched sample for a few minutes corresponds to the calcium in the hydroxyapatite. Main peaks which appeared in Ca $2p_{1/2}$ and Ca $2p_{3/2}$ orbital of sintered hydroxyapatite plate

coated with PAA correspond to the calcium in the calcium polyacrylate which is a product of the chemical reaction of polyacrylic acid with calcium in the sintered hydroxyapatite. This results agree with ATR study of infrared spectroscopic method to research the chemical reaction at the interface of PAA and hydroxyapatite⁽¹⁴⁾. In this infrared spectroscopic experiment, hydroxyapatite plate and human tooth enamel plate coated with PAA were quickly loaded on to the ATR prism, and then, a few spectra of reaction between the plates and PAA near the interface were recorded. The absorption bands of the asymmetric C=O stretch at 1530cm^{-1} and the symmetric C=O stretch at 1400cm^{-1} appeared, these two absorption bands were the results of the formation of calcium polyacrylate. These results are in good agreement with previous works⁽²⁾⁽⁹⁾. Crisp concluded from their infrared spectroscopic study that calcium polyacrylate salt are purely ionic and calcium ions are bound to the polyanion chains by general electrostatic interactions⁽²⁾. Our results of ESCA and ATR of infrared spectroscopic measurement on the nature of the chemical interaction at the interface of polyacrylic acid and hydroxyapatite plate support the McLeans' adhesive model⁽¹⁵⁾ which is shown in Fig. 4.

In cementation during dental treatment an aqueous solution of PAA is mixed with the cement powder. During mixing, free carboxylate groups of PAA react with metal ions in the cement powder to form some salts⁽²⁾. The amount of free carboxylate groups decreases rapidly with time after mixing⁽¹⁴⁾ as shown in Fig. 5. When tooth substance and metal contact with the PAA after mixing of the cement, there is a diminished number of free carboxylate groups available to react with the tooth substance and the metal. It is expected that the large majority of car-

boxylate groups of PAA react with metal ions in the cement powder, and the minor part of carboxylate groups of PAA react with the tooth substance and metal restoration. This might be able to explain why the adhesive force of the cement is not as that suggested by the chemical reaction of PAA with sintered hydroxyapatite plate demonstrated by the ESCA measurement of this study.

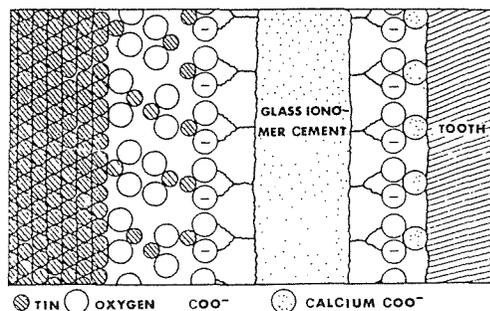


Figure 4. Schematic illustration of the bonding of glass-ionomer cement to tooth substance.

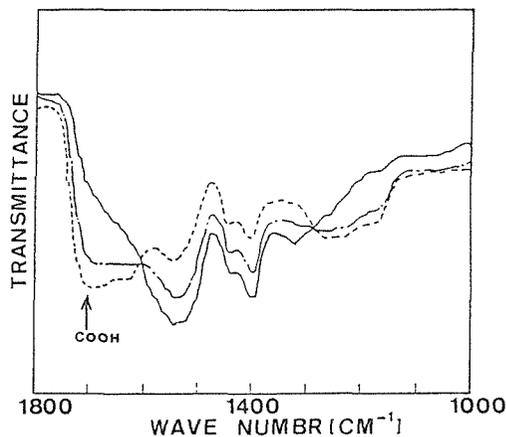


Figure 5. IR spectra of a commercial dental cement (SANKIN : CARLON, Sankin Co., Osaka) at 1 min (-----), 4 min 10 sec (— · —) and 10 min (——) from the commencement of mixing in setting process.

5 . Conclusion

ESCA measurement of sintered hydroxyapatite plate coated with PAA was performed to examine the mechanism of adhesion combined with Ar⁺ ion beam etching. The results of the measurement showed that calcium in hydroxyapatite plate reacted with PAA to form the calcium polyacrylate. This chemical reaction contributes to the strong adhesive force of these cements to the tooth enamel.

Acknowledgment

The authors wish to thank Mr H. Sekiguchi and Mr S. Aikawa for assistance of ESCA measurements, Mr I. Ohtsuka for helpful discussion.

References

- (1) S. Crisp and A.D. Wilson, Part 1: J. Dent. Res., Vol.53, p.1408(1974).
Part 2: J. Dent. Res., Vol.53, p.1414(1974).
Part 3: J. Dent. Res., Vol.53, p.1420(1974).
- (2) S.Crisp, H. J. Prosser and A. D. Wilson, J.Mater. Sci., Vol.11, p.36(1976).
- (3) D. C. Smith, Br. Dent. J., Vol.125, p.381(1968).
- (4) D. C. Smith, J. Biomed. Mater. Res. Symp., Vol.1, p.189(1971).
- (5) H. P. Gregor, L.B.Luttinger and E. M. Loebel, J. Phys. Chem., Vol.59, p.34(1955).
- (6) H. P. Gregor, L. B. Luttinger and E. M. Loebel, J. Phys. Chem., Vol.59, p.990(1955).
- (7) A. Ikegami, J. Polym. Sci. A, Vol.2, p.907 (1964).
- (8) A. L. Jacobson, J. Polym. Sci., Vol.57, p.321 (1962).
- (9) D. R. Beech, Arch. Oral. Biol., Vol.17, p. 907(1972).
- (10) M. Klasson, J. Hedman, A. Berndtsson, R. Nilson and C. Nordling, Physica Scripta, Vol.5, p.93(1972).
- (11) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordling and K. Hamrin, *Almovist & Wiksells Boktryckeri Ab., Uppsala*, p.76 (1967).
- (12) T. Nasu, J. Biomed. Mat.Res., Vol.20, p.347 (1986).
- (13) H. Aoki, M. Ebihara and M.Inoue, J. Jap. Soc. Dent. Appar. Mat., Vol17, p.200(1976).
- (14) T. Nasu, K. Nagaoka, I. Ohtsuka and H. Aoki, Bull. Yamagata Univ. (Eng.), Vol. 18, p.25(1984).
- (15) J. W. McLean, Operative Dent., Vol.2, p. 130(1977).