Colloid Polym Sci 277:382–387 (1999)
© Springer-Verlag 1999

SHORT COMMUNICATION

M. Es-Souni
R. Zimehl
H. Fischer-Brandies

Microscopic and electron spectroscopic characterization of dental enamel surfaces

Received: 6 November 1998
Accepted in revised form: 3 December 1998

M. Es-Souni (✉) · H. Fischer-Brandies
Clinic of Orthodontics
Christian Albrecht University
Arnold-Heller-Strasse, D-24105 Kiel
Germany
e-mail: fi-br@kfo-zmk.uni-kiel.de
Tel.: +49-431-5972881

R. Zimehl
Institute of Inorganic Chemistry
Christian Albrecht University
Arnold-Heller-Strasse, D-24105 Kiel
Germany

Abstract The effects of surface pretreatment on the topography and composition of dental enamel surfaces of extracted bovine teeth have been investigated by scanning electron microscopy and X-ray photoelectron spectroscopy. Surface pretreatment with a solution of benzoic acid in acetone does not change the topography of the surface; it leads to enrichment of calcium and, to a lesser extent, phosphorus at the enamel surface. The higher adhesion strength reported between enamel surfaces pretreated with benzoic acid in acetone and glass ionomer cement might be explained in terms of a greater number of chemical bonding sites due to the enrichment of calcium and phosphorus at the surface.

Key words Enamel conditioning – Surface analysis – Benzoic acid – Analytical electron microscopy – X-ray photoelectron spectroscopy

Introduction

Glass ionomer cements (GIC) are largely used as fixation materials for orthodontic treatment. They are assumed to bind chemically to the enamel surface [1]. Despite their positive properties such as the possibility to release fluoride ions, thus having preventive action on caries [2–4], they still have not found application in bracket fixation, because of their poor adhesion strength [5, 6]. However, it has been demonstrated that pretreatment of dental enamel with suitable substances such as polyacrylic acid (PAA) [6], benzoic acid in acetone (BAA) and salicylic acid in acetone (SAA) [7] results in improved bond strength between enamel and GIC. The positive effect of PAA conditioning with respect to the enhanced adhesion of GIC to enamel was explained in terms of the ability of PAA to interact with the substrate in order to promote wetting, cleaning and smoothing of the surface [6]. PAA was also supposed to adhere by adsorption at the surface, without forming soluble complexes, and thus dissolving the calciferous substrate [6]. The mechanism of adhesion of polyelectrolyte ions of the cement to hydroxyapatite, the main constituent of enamel, was investigated using infrared and optical emission spectroscopy [1]. It has been shown that the adhesion results from the displacement of phosphate and Ca ions by carboxylate groups of the polyacrylate ions [1]. PAA conditioning of enamel surfaces is supposed to promote these mechanisms by assuring intimate intermolecular contact between cement and enamel [6].

Fischer-Brandies et al. [7] reported a significant improvement in bond strength between GIC and enamel by introducing BAA and SAA as conditioning solutions. So far these conditioners have only been studied as to their effect on the mechanical strength of the bracket-GIC-dental enamel bonds [7].

The aim of this paper is to contribute to the understanding of the chemical nature of the interaction between BAA as a conditioning agent and enamel, and to discuss the consequences of this type of conditioning on GIC-enamel bonds. For this purpose the topography of conditioned and untreated enamel surfaces were studied by scanning electron miroscopy (SEM). The chemical composition of the outermost surface layers was investigated using a powerful surface analysis method: X-ray photoelectron spectroscopy (XPS). As it is known that adhesion of GIC to bovine and human enamel is very similar [8], bovine enamel was chosen as the substrate.

Materials and methods

Freshly extracted bovine mandibular incisors were used. Only teeth with intact enamel, this means, no caries or visible enamel fractures, were chosen. After removal of the root and the adherent tissue, the crown was thoroughly washed, first with tap water and then with distilled water. The material was stored in 0.9% NaCl solution which was changed weekly. Prior to SEM or XPS studies the labial side of the tooth was cut parallel to the enamel surface by a diamond saw with water cooling. Tooth pieces with a thickness of 2–3 mm and an enamel surface of about 0.7 cm^2 were obtained. The surfaces were then cleaned with a fluoride-free ready-to-use pumice paste (PELL-EX, Haweneos Dental) and a soft rubber cup. For SEM investigations the tooth slabs were additionally divided into four thin sections and only the second and third quarter were studied. Parts of these surfaces were ground on 1200-grade silicon carbide waterproof paper, cleaned ultrasonically in distilled water and then subsequently rinsed with distilled water. Cleaned and dried substrates were then exposed for 2 min to the action of acetone or a solution of benzoic acid (3% weight in acetone). After exposure, the enamel was abundantly washed with distilled water and subsequently dried with compressed air. For XPS investigations a native surface was used for comparison.

Topographical SEM analyses of the enamel surfaces were carried out in an analytical SEM (XL-30, Philips). The specimen was sputter-coated with gold in an EMITECH sputter coater prior to SEM analysis. XPS analysis of the conditioned, reference (i.e. polished, nonconditioned) and native (nonpolished, nonconditioned) surfaces were conducted in an OMICRON system under an ultra-high vacuum of 10^{-9} mbar, using a Mg Kα soft X-ray source. The peaks of the following elements were analysed: P, Ca, C, and O. Due to charging effects the peak positions were corrected with the energy of the 1*s* C peak at 284.5 eV as the reference. Background subtraction and area calculations of the different peaks were carried out with the software supplied.

Results

SEM investigations

The topography of the polished part of the enamel surface is shown in Fig. 1. Conditioning with acetone or BAA did not lead to visible etching, and the surface topography remained practically unchanged (Figs. 2, 3a). Due to the fact that bovine enamel surfaces show irregularities and pits, a reference surface was produced via grinding with 1200-grade abrasive paper and subsequent conditioning. The surface thus obtained showed grooves spotted with debris due to the grinding, but no etching effects could be observed, as already mentioned for the polished substrates (Fig. 3b).

XPS investigations

The XPS measurements (C, O, P and Ca) only show a substantial shift of the O peak (Fig. 4a–d); polishing and surface treatment with acetone or BAA leads to a shift of about 2 eV towards lower binding energies. As indicated by the C 1*s* peak of the native surface, C is essentially present as hydrocarbons at 284.5 eV, but may also be present as elementary C as a surface contaminant. A

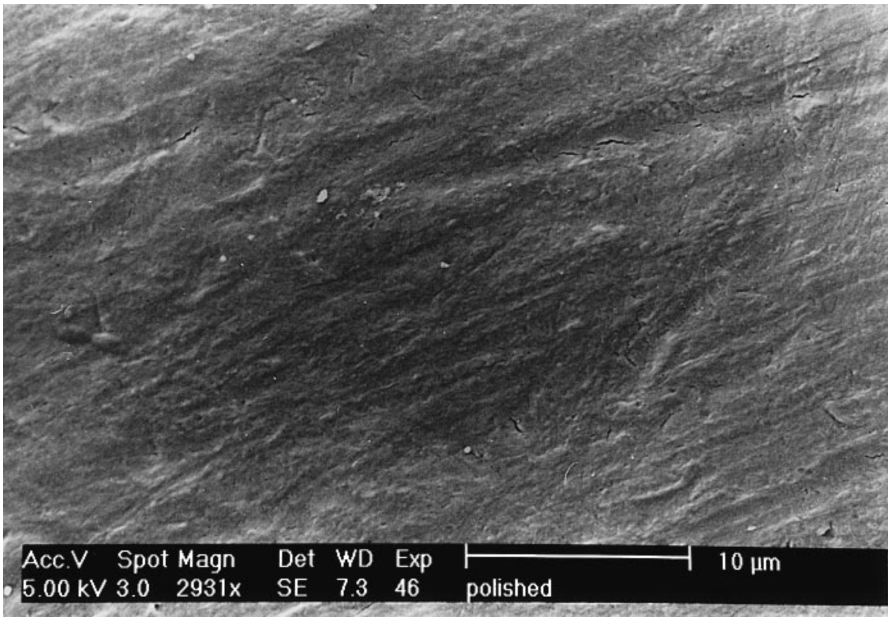

Fig. 1 Scanning electron (*SE*) micrograph of a polished enamel surface

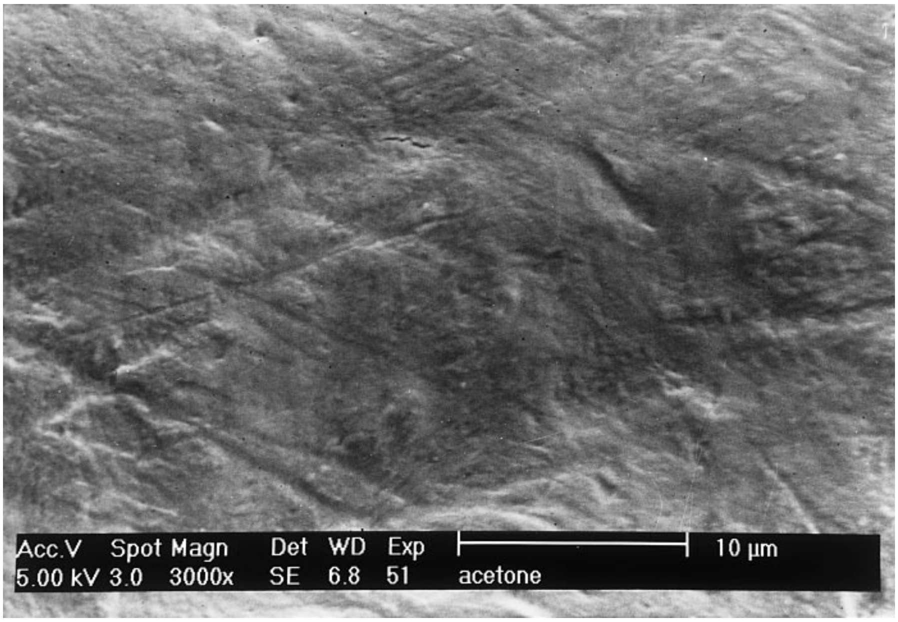

Fig. 2 SE micrograph of a polished and acetone-treated enamel surface

shoulder is seen at a higher binding energy, which upon deconvolution of the peak (Fig. 4e) shows a maximum at 287.5 eV. This indicates binding to O, likely as carboxyl or carbonate, and with S or N [9]. The surface treatment, like polishing or conditioning with acetone, leads to the gradual, and with BAA, complete disappearance of this shoulder . The slight energy shifts observed for Ca from higher to lower binding energies, for the acetone- and BAA-treated surfaces in comparison to the native one, denote the gradual elimination of the outermost native surface layer; the Ca $2p_{1/2}$ $2p_{2/3}$ binding energy shifts towards the energy of Ca in CaO [10]. The observed energy shifts for P are small and all lie in the energy range of phosphate [10].

Surface treatment substantially increases the intensities of Ca, P and O with respect to the polished surface (Fig. 4f). The carbon peak area of the acetone- and BAA-treated surfaces decreases. The area of the C peak is highest on the native surface. Acetone increases the area of the Ca peak by 20%, whereas enrichment of about 60% is achieved by BAA conditioning. In the native state the Ca peak intensity is weaker than that of the polished surface because of attenuation effects due to the outermost organic layer. In comparison to the polished surface the relative intensity of the P peak increases on the BAA-treated surface by about 20%.

Discussion

The mechanism of adhesion of GIC to tooth surfaces has been studied by Wilson et al. [1] using PAA, representing the reactive part of the cement, and hydroxyapaptite, the main constituent of dental substance as a model system. Binding was achieved by carboxylate groups penetrating the apatite matrix and displacing Ca and phosphate ions. Hotz et al. [5] and later Powis et al. [6] showed that efficient binding requires treatment of the dental surface by conditioners able to improve its wettability, cleanliness and smoothness. Most of the conditioners tested were aqueous solutions of acids, and only topographical effects on the treated surfaces were investigated. Fischer-Brandies et al. [7] showed that the adhesion strength of a GIC to bovine enamel treated with solutions of aromatic acids such as benzoic and salicylic acid in acetone could be improved by 38% compared to PAA-treated enamel. As already mentioned, the topography of the smooth polished enamel surface was not affected by conditioning and no microetching could be observed with BAA solutions, neither on ground nor on polished enamel. Thus, from the topographic point of view BAA-treated surfaces are similar to those treated with PAA, and the higher adhesion strength cannot be due to some additional mechanical retention. The reported higher adhesion strength might be caused by the altered surface composition of the enamel. The results of the XPS measurements show that BAA conditioning led to a superficial enrichment in Ca (60%) and to a lesser extent in P (20%), and to a substantial decrease in C. The decrease in C can be related to the dissolution of organic pellicle residues by washing with acetone, which results in an increase in surface free energy; this is expected to improve the substrate wettability [11]. Thus polishing

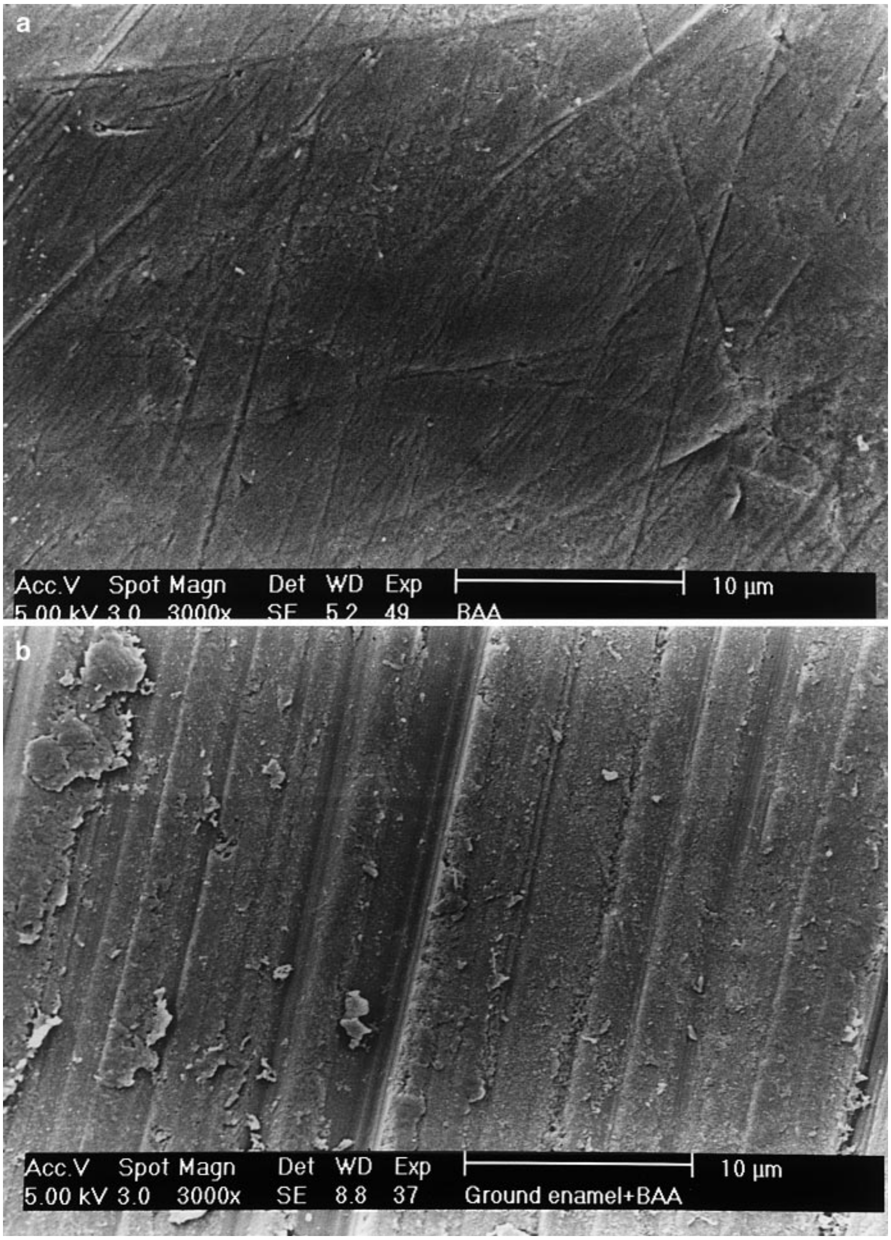

Fig. 3 **a** SE micrograph of a polished and benzoic acid in acetone (*BAA*) treated enamel surface. No etching effects appear **b** SE micrograph of a ground and BAA-treated enamel surface. Grooves spotted with debris due to grinding appear, but no etching effect is observable

and treating enamel with acetone-containing solutions improves the surface cleanliness and the wettability of enamel; both aspects are necessary conditions for good contact, and thus adhesion, between substrate and GIC. These conditions, however, are not sufficient for good adhesion between GIC and enamel, since conditioning with acetone alone does not improve bonding strength [7]. The combined effects of BAA by cleansing and changing the surface chemistry are more efficient for establishing a higher adhesion strength.

The superficial enrichment in phosphate and Ca after BAA treatment increases the number of binding sites for PAA of the cement, and thus improves the adhesion strength of the GIC to enamel.

Conclusion

The improved adhesion strength of GIC on polished and BAA-conditioned surfaces results from combined actions on superficial cleanliness, wettability and surface chemistry; in this respect the superficial enrichment in Ca and P is considered to increase the number of binding sites of the cement for PAA.

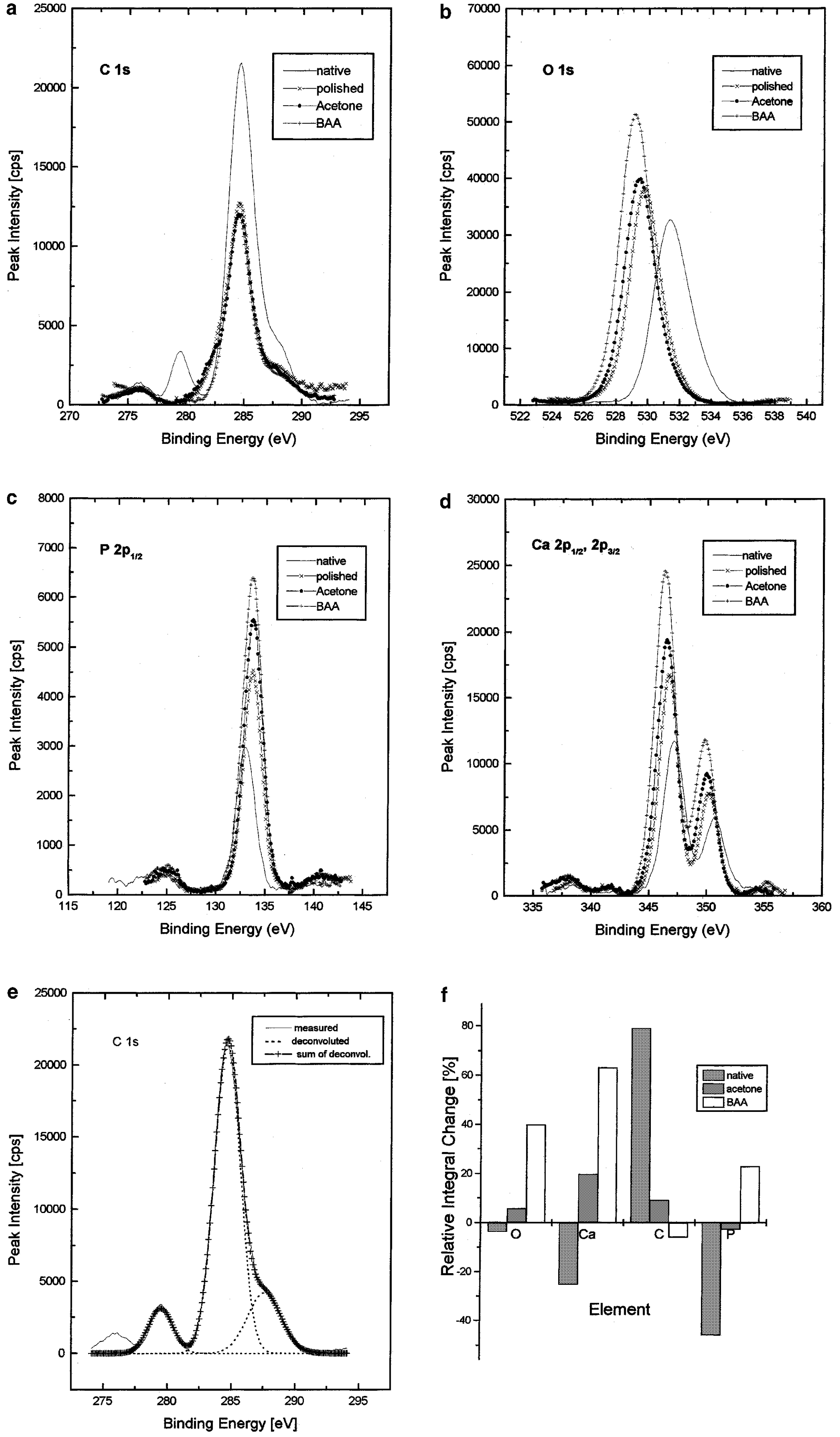

Fig. 4a–f Results of the X-ray photoelectron spectroscopy (*XPS*) analyses of different elemental peaks after surface pretreatment. **a** carbon 1*s*; **b** oxygen 1*s*; **c** phosphorus $2p_{1/2}$; **d** calcium $2p_{1/2}2p_{3/2}$; **e** deconvolution of the carbon peak of the native enamel surface shown in **a**; **f** relative surface excess concentration of the different elements studied by XPS

Acknowledgements The authors are grateful to K. Behnke, Technical Faculty of the Christian Albrecht University of Kiel, Germany, Department of Materials Science, for conducting the ESCA experiments and to F. Faupel for permission to use the ESCA equipment. Thanks are due to M. Hannig, Clinic of Operative Dentistry and Parodontology of the Christian Albrecht University of Kiel, Germany, for helpful discussion. The Deutsche Forschungsgemeinschaft is gratefully acknowledged for financial support of this work.

References

1. Wilson AD, Prosser HJ, Powis DM (1983) J Dent Res 62:590
2. Fischer-Brandies H, Kluge G, Theusner J, Häusler K (1991) Dtsch Zahn-Mund-Kieferheilkd 79:349
3. Kidd EAM (1978) Br Dent J 144:139
4. Wesenberg G, Hals E (1980) J Oral Rehabil 7:35
5. Hotz P, McLean JW, Sced I, Wilson AD (1977) Br Dent J 142:41
6. Powis DR, Folleras T, Merson SA, Wilson AD (1982) J Dent Res 61:1416
7. Fischer-Brandies H, Scherer R, Theusner J, Häusler (1992) Fortschr Kieferorthop 53:131
8. Nakamichi I, Iwaku M, Fusayama T, (1983) J Dent Res 62(10):1076
9. Handbook of X-ray photoelectron spectroscopy (1992) Perkin Elmer Corporation, Physical Electronic Devision, Edenprairie, Minn
10. Wagner CD (1983) In: Briggs D, Seah MP (ed) Auger and photoelectron energies and the Auger parameter: a data set. Practical surface analysis by Auger and X-ray photoelectron spectroscopy. Wiley, London, p 477
11. Busscher HJ In: Schrader ME, Loeb GI (ed) Wettability of surfaces in the oral cavity. Modern approaches to wettability. Plenum, New York, p 249