Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
JNMU
Journal of Nanjing Medical University, 2007, 21(5):337–340
www.elsevier.com/locate/jnmu
Research Paper

Effects of plasma treatment time on modification of acrylic denture material ☆

Huaiqin Zhang[a,*], Linjuan Liu[a], Jianglin Fang[b]
[a]*Research Institute of Stomatology, Nanjing Medical University, Nanjing 210029, Jiangsu Province, China;*
[b]*Modern Analysis Centre, Nanjing University, Nanjing 210093, Jiangsu Province, China*
Received 23 May 2007

Abstract

Objective: To study the relationship between plasma treatment time and efficacy. **Methods:**Test specimens were prepared from an acrylic resin denture material in the size of 2 mm × 10 mm × 10 mm. Plasma treatment was carried out on the surface of Polymethyl methacrylate(PMMA) at different time. XPS studies, IR spectra studies and measurement of wetting angle were performed. **Results:** XPS showed the peak corresponding to C-O getting higher as the treatment proceeded, however at 120 seconds, the peak did not increase any longer and partly crossed with the peak at the duration of 60 seconds. IR spectra showed the wave corresponding to C-H was reduced as O_2-plasma treatment proceeded, and then changed little. Wetting angle initially decreased dramatically, however, as the reaction proceeded, wetting angle increased slightly. **Conclusion:**Equilibrium was reached for introducing oxygen-containing groups and changing of C-H. As the treatment proceeded, wetting angle increased slightly.

Keywords: plasma; modification; acrylic denture material

INTRODUCTION

Because of the friable nature of the supporting mucosa, force concentration can result in tissue trauma and sore spots. As a result of these conditions, patients frequently do not wear dentures because of the discomfort that accompanies their use. To alleviate the possibility of discomfort arising from denture base force transfer to oral mucosa, many studies have been done[1-2]. Denture soft lining materials have been applied to the tissue surface of dentures to reduce local pressures and improve retention of the prosthesis[3-5]. One of the most serious problems with soft lining materials is the failure of adhesion between the soft lining materials and the denture base[6].

For the reasons of low surface energy, chemical inertness, surface contamination and weak boundary layer, polymer surface often presents low wettability and dissatisfied adhesion characteristics. Therefore, the surface of polymer needs to be modified.

The following methods are commonly used for polymer surface modification: chemical modification; actinochemistry modification; surface modification by modifying agent; dynamochemical treatment; heat treatment; coupling agent modification and chemical modification by radiation.

Some of above-mentioned methods are too complicated to operate, and some produce a great deal of waste liquid during the process, which is harmful to health and environment. Low temperature plasma is a new subject based on the development of physics, chemistry, electronics and the vacuum technique. Low temperature plasma has characteristics of low reaction temperature, being easy to handle, low cost and without pollution to the environment[7-8]. Plasma treatment has previously been used in surface modification of medical devices and materials, by improving biocompatibility

☆ This work was supported by Science Fund of Department of Education of Jiangsu Province(06KJD320125)
*Corresponding author.
E-mail address: dentzhq@sina.com.cn.

and adhesion characteristics[9-11].

MATERIALS AND METHODS

The specimens were prepared with acrylic resin denture material(Zi Ran, Nissin, China) in the size of 2 mm×10 mm×10mm. The surfaces of all the specimens were smoothed with aluminum oxide paper (Suzhou sand-paper factory) in 280 and 800 mesh, then washed with distilled water and dried in air. The specimens were placed in a glass tubular reactor. The reactor was evacuated from the right side using rotary vacuum pump until a pressure of 0.01 mmHg achieved. Oxygen gas was then introduced into the reactor to displace the residual gases. Evacuation and introduction were repeated several times. Finally, the pressure was controlled at 0.3 mmHg by appropriate opening of the inlet valve. Imposition of power of 60 w created the condition, under which plasma treatment was carried out.

① X-ray photoelectron spectroscopy studies:The power of 60 w was imposed for O_2-plasma treatment with different treatment time(10s;30s;60s;120s), 2 specimens in each group. X-ray photoelectron spectroscopy studies were performed on an electron spectrometer (ESCALAB MK-Ⅱ VG Corp, U.K.), with MgKa X-rays(12.5 kv) having a background pressure lower than 1×10^{-7} Torr.

② IR spectra studies:The power of 60 w was imposed for O_2-plasma treatment with different treatment time (0.5 min; 1 min; 2 min; 4 min; 8 min), 2 specimens in each group. IR spectra studies were performed on an IR spectrometer(NEXUS870, NICOLET Corp, U.S.).

③Change of wetting angles: 42 specimens were prepared from an acrylic resin denture material in the size of 2 mm×10 mm×10 mm and randomly divided into 7 groups(6 specimens in each group). O_2-plasma treatment time was from 0 to 6 min.Wetting angles were measured with goniometer(JJC-1, Changchun experiment instrument Corp, china). The measurements were made with doubly distilled water at 5 points by the static sessile drop method.

RESULTS

Fig 1 is C_{1S} XPS of control and O_2-plasma treatment groups on the surface of PMMA. The peak corresponds to structure of C-C at 284.5ev and the peak corresponds to structure of C-O at 287eV. At 287eV, the peak got higher as the treatment proceeded, however at 120 seconds, the peak did not increase any longer and crossed with the peak at the duration of 60 s. ***Fig 2*** was amplified part of C_{1S} XPS. ***Fig 3*** is IR spectra of control and O_2-plasma treatment groups on the surface of PMMA. At 2960-2870 cm^{-1}, the wave corresponding to C-H was reduced as O_2-plasma treatment proceeded, and then changed little. ***Fig 4*** showed the relationship between wetting angle and treatment time. Wetting angle initially decreased dramatically, however, as the reaction proceeded, wetting angles increased slightly.

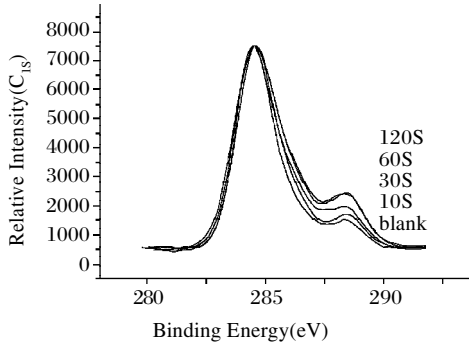

Fig 1 C_{1S} XPS of different O_2-plasma treatment duration

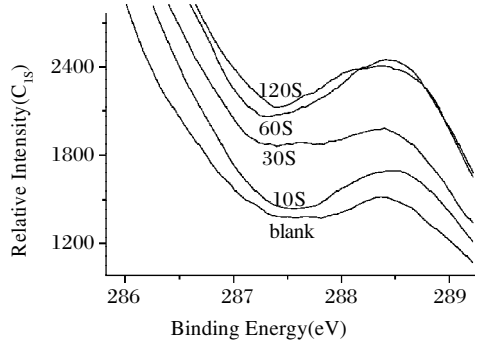

Fig 2 Amplified part of C_{1S} XPS of different O_2-plasma treatment duration

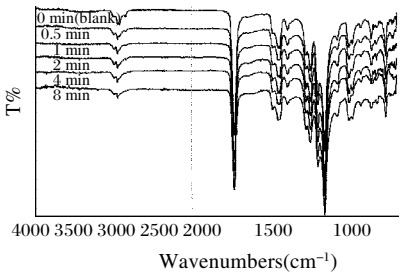

Fig 3 IR spectra of different O_2-plasma treatment duration

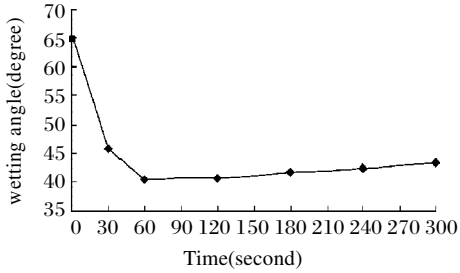

Fig 4 Graph of wetting angle change with the treatment time

DISCUSSION

The energy of particles in plasma is higher than the energy of ordinary bond (C-H; C-N; C-Cl; C-F; C=O; C-C; C=C; C ≡ C). This means plasma is powerful enough to break or realign the various chemical bonds, which make macromolecule degraded. The low temperature plasma can stimulate molecules and atoms effectively without damage of the molecules of the polymer[12,13].

Wettability is usually referred to the wetting process among liquid/air/solid. The wetting angle provides a quantitative measure of the wetting process[14,15]. A liquid is considered to be wetting a surface when θ is < 90 degrees, and is considered nonwetting when θ is > 90 degrees. A wetting angle $\theta = 0$ degree corresponds to perfect wetting, in which the drop spreads to from a film on the surface[16]. The smaller the wetting angle, the greater the wettability[17]. The ability of a solid to become wet is proportional to its surface energy. If adhesion between solid and liquid is stronger than cohesion within liquid, the solid can be wetted. On the contrary, the solid cannot be wetted. The wettability characters on the surface of polymer can be summed up as: The wettability of a polar compound is better than that of a compound without polar groups; Wettability of a polymer has relation with its composition. Adding other atoms into the chain of carbon can improve wettability of polymer remarkably, except the F atom. The order of atoms improving wettability is H<Cl<Br <I<O<N; Wettability of polymer is decided by character and arrangement of atoms or groups on the surface, with little relationship to bulk.

Plasma treatment can change chemical composition, increase surface energy, eliminate contamination and a weak boundary layer on the surface of the polymer, so as to improve its wettability and adhesion[18,19]. In this study, the peak corresponding to C-O at 287eV became higher as treatment proceeded, indicating a large number of oxygen-containing groups were introduced onto polymer surface[20,21]. At the duration of 120 seconds, the peak did not increase any longer and partly crossed with the peak at 60 seconds. The prolonged period of exposure leaded to excessive surface degeneration, which spoiled the surface properties due to accumulating of degenerated remnants[22]. This explained the reason for the initial decrease in wetting angle and then slight increase. IR spectra on O_2-plasma treated surface showed a similar tendency. At 2960-2870cm^{-1}, the wave corresponding to C-H was reduced as O_2-plasma treatment proceeded, and then changed little, indicating decrease in structure of C-H and increase in structure of C-C, which meant the cross-linking structure was formed on the surface of PMMA. Cross-linking structure is a kind of dense layer and effective in eliminating weak boundary layer on the surface of PMMA.

References

[1] Chun-bo Tang, Jian-ming Ma, Xin Tong, Jian-long Jing, Yue-qing Zhou. Clinical observation and evalution of implant-supported overdentures in 20 patients. *ACTA Universitatis Medicinalis Nanjing* 2005;25:661-3.

[2] Jun Sun, Ke Zhao, Xiang-rong Cheng. Effect of Comfort-DA denture adhesive on masticatory efficiency and haemolysis test.*ACTA Universitatis medicinalis Nanjing* 2003; 23:161-2.

[3] Sarac D, Sarac S, Basoglu T, Yapici O, Yuzbasioglu E.The evaluation of microleakage and bond strength of a silicone-based resilient liner following denture base surface pretreatment.*J prosthet Dent* 2006;95:143-51.

[4] Mese A, Guzel KG, Uysal E.Effect of storage duration on tensile bond strength of acrylic or silicone-based soft denture liners to a processed denture base polymer.*Acta Odontologica Scandinavica* 2005;63:31-5.

[5] Garcia RM, Leon BT, Oliveira VB, Del Bel Cury AA. Effect of a denture cleanser on weight, surface roughness, and tensile bond strength of two resilient denture liners. *J Prosthet Dent* 2003;89: 489-94.

[6] Minami H, Suzuki S, Ohashi H, Kurashige H, Tanaka T. Effect of surface treatment on the bonding of an autopolymerizing soft denture liner to a denture base resin.*Int J Prosthodont* 2004,17:297-301.

[7] Sato M, Slamovich EB, Webster TJ. Enhanced osteoblast adhesion on hydrothermally treated hydroxyapatite/titania/poly (lactide-co-glycolide) sol-gel titanium coatings. *Biomaterials* 2005;26: 1349 - 57.

[8] Yahia L, Lombardi S, Selmani A, Drouin G, Hlaouti M. Effect of plasma treatment on tribological properties of synthetic ligaments. *Biomed Mater Eng* 1994;4: 347-56.

[9] Chen-Yang YW, Chen CW, Tseng SC, Huang J, Wu YZ. Surface modification of bi-axially expanded poly (tetrafluoroethylene) by plasma polymerization of ethylene. *Surface and Coatings Technology* 2004, 17: 148-56.

[10] Lv Q, Cao C, Zhu H. Blood compatibility of polyurethane immobilized with acrylic acid and plasma grafting sulfonic acid. *J Mater Sci Mater Med* 2004,15: 607-11.

[11] Assero G, Satriano C, Lupo G, Anfuso CD. Pericyte adhesion and growth onto polyhydroxymethylsiloxane surfaces nanostructured by plasma treatment and ion irradiation. *Microvasc Res* 2004,68: 209-20.

[12] Lim H, Lee Y, Han S, Kim Y, Song JM, Kim JS. Wettability of Poly (Styrene-co-acrylate) ionomers improved by Oxygen-Plasma Source ion implantation. *J Polymer science: Part B: Polymer physics* 2003; 41: 1791-7.

[13] Vassilakos N, Fernandes CP, Nilner K. Effect of plasma treatment on the wettability of elastomeric impression materials. *J Prosthet Dent* 1993;70:165-71.

[14] Oh W, Shen C,Alegre B,Anusavice KJ. Wetting charcteristic of ceramic to water and adhesive resin. *J Prosthet Dent* 2002;88:616-21.

[15] Weikart CM, Miyama M, Yasuda HK. Surface modification of conventional polymers by depositing plasma polymers of trimethylsilane and of trimethylsilane + O_2. *J Colloid Interface Sci* 1999;211: 28-38.

[16] Hong-wei Li , Dong-hua Zhang, Bing Qi, Yu-ming Wen, Chang-mei Wang. Study on the celludlar affinity of PLGA.. *ACTA Universitatis Medicinalis Nanjing* 2005;25:959-61.

[17] Erkut S, Can G.. Effects of glow-discharge and surfactant treatments on the wettability of vinyl polysiloxane impression materials. *J Prosthet Dent* 2005;93: 356-63.

[18] Huai-qin Zhang, Yong-lie Chao. Effect of treatment with Ar plasma on the surface of soft-lining material. *ACTA Universitatis medicinalis Nanjing* 2005; 25:65-6.

[19] Gray JE, Norton PR, Griffiths K. Surface modification of a biomedical Poly (ether) urethane by a remote air plasma. *Applied surface science* 2003,217: 210-22.

[20] Park SJ, Lee HY. Effect of atmospheric-pressure plasma on adhesion characteristics of polyimide film. *J Colloid Interface Sci* 2005; 285: 267-72.

[21] Chen M, Zamora PO, Som P, Pena LA, Osaki S.Cell attachment and biocompatibility of polytetrafluoroethylene (PTFE) treated with glow-discharge plasma of mixed ammonia and oxygen. *J Biomater Sci Polym Ed* 2003;14: 917-35.

[22] Hesby RM, Haganman CR, Stanford CM. Effects of radiofrequency glow discharge on impression material surface wettability. *J prosthet Dent* 1997; 77: 414-22.