



Interaction of Water and Fiber Free and Fiber Reinforced Acrylic Resins: Studied by 400 MHz NMR

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(Received: 20 January 2011;

Accepted: 30 June 2011)

AJC-10121

There is no report is available on the interaction of polymerized acrylic resin materials with water studied by high resolution NMR. In this study, the chemical shifts of NMR peaks of water interacting with different types of polymerized acrylic resin materials were compared. Two different types of polymers obtained by heat and microwave, were selected. Each NMR sample was prepared by mixing the dusty materials and 1 mL of a mixture of H₂O (80 %) and D₂O (20 %). The water proton signals in samples were measured by 400 MHz NMR. The data was divided into four groups. The chemical shifts of microwave acrylic resin (group 3) was higher than that of microwave acrylic resin reinforced with glass fibers (group 4), while the chemical shift of heat cured acrylic resin (group 1) was higher than that of heat cured acrylic resin reinforced with glass fibers (group 2). Furthermore, the chemical shifts of material polymerized by microwave are higher than those polymerized by injection (group 3 > group 1, and group 4 > group 2). Data shows that different type of polymerized acrylic resin materials can be differentiated by chemical shift measurements.

Key Words: Acrylic resins, Fiber reinforced, NMR, Chemical shift.

INTRODUCTION

Acrylic resins are widely used in dentistry. One of the properties of acrylic resins is water sorption and release, which causes dimensional instability, thereby subjecting the material to internal stresses that may result in crack formation and, eventually, fractures of the denture¹⁻⁴. Because water interacts with the polymer chains, it may produce some effects such as reversible loosening or effective plasticization of the structure, solvation or reversible rupture of weak interchain bonds and irreversible disruption of the polymer matrix. Therefore, the water sorption and solubility are the critical problems that affects durability of the resins^{3,4}. This behaviour affects dimensional behaviour and denture stability. Therefore, water sorption and solubility of these materials should be as low as possible^{4,5}. Many studies on the water sorption of denture resin have been conducted and concluded that sorbed water would cause the decrease of mechanical properties^{2,6-10}.

The water sorption and water solubility were determined according to the International Standards Organization (ISO) standards 1567:1999¹¹. According to this specification, water sorption should not exceed 32 µg/mm³ for heat-cured or self-cured materials. The loss in mass per unit volume (soluble material) should not exceed 1.6 µg/mm³ for heat-cured and 8.0 µg/mm³ for self-cured materials^{11,12}.

The recognition of nuclear magnetic resonance (NMR) spectra is based on chemical shift, which is a shift in an NMR signal position caused by local electronic currents¹³. The line width studies of NMR signals are also commonly used for providing information about environmental change of water¹³. Actually, the chemical shift studies are being used in medicine and dental medicine for the recognition of the environmental properties of the nucleus under question¹⁴⁻¹⁷. To the best of our knowledge, studying water-acrylic interaction through the chemical shift has not been made so far. The aim of the present study is to compare the interaction of water with solid for different type of polymerized acrylic resin materials.

EXPERIMENTAL

Two commercial acrylic resin materials (with and without fiber reinforced) were tested. The products and manufacturers of the materials are listed in Table-1.

Stainless mould specimens: Fourty stainless mould was fabricated each 50 mm long, 10 mm wide and 3 mm thick. The stainless moulds were placed in denture flasks and improved dental stone in to denture flasks. After the dental stone sets, the flask was open and the stainless flasks were gently removed from the stone compartments. The mould cavities obtained were used to prepare acrylic resin test

TABLE-1
TYPE OF ACRYLIC RESIN MATERIALS

Product name	Type	Manufacturers
QC 20	Heat cured acrylic resin	AD International Ltd, De Trey Division, Surrey, UK
Shera-Med 2000	Microwave cured acrylic resin	NW 2000, Dental-Werkstoffe, Lemförde, Germany

specimens. The four experimental groups consisted of heat cured acrylic resin, microwave cured acrylic resin and the same resin reinforced with glass fibers. Ten specimens were fabricated in a standardized fashion for each experimental group.

Acrylic resin specimens: Group 1 specimens were made with heat cured acrylic resin (QC-20, AD International Ltd., De Trey Division, Surrey, UK). A mixture of monomer and polymer in a ratio of 1:2,4 by weight was allowed to reach the double stage and was then kneaded and placed in the mould. Trial closure was performed with a hydro press at 40 000 N (Ka Vo EWL, Leutkirch, Germany). The flask was clamped and low pressure was maintained for 40 min to allow the proper penetration of monomer into the polymer, the even flow of the material and the outward flow of excess material. After the polymerization cycle was complete, the flask was allowed the cool to room temperature in a water bath before deflasking. The all acrylic specimens were retrieved, finished and polished in the same manner.

Group 2 specimens were made with heat cured acrylic resin (QC-20, AD International Ltd., De Trey Division, Surrey, UK) of the same dimensions as group 1 that were reinforced with glass fibers (Glass Fiber Co., Kocaeli, Turkey). The glass fibers were 5-10 μm thick and were cut to 2.5 mm lengths. The acrylic resin and fiber specimens (2 % by weight) were prepared by cutting fiber slightly short of the size of the slots. The cut fibers were soaked in monomer for 10 min to allow for better bonding with the acrylic resin. The fibers were removed from the monomer and the excess liquid was allowed to dry. The resin and fibers were mixed thoroughly to disperse the fibers. After reaching the dough stage, the mixture was kneaded and packed into the prepared mould. The specimens were polymerized and recovered in the same manner as group 1.

Group 3 specimens were made with microwave acrylic resin (Shera-Med NW 2000, Dental-Werkstoffe, Lemförde, Germany) the specimens were invested in a three-part polycarbonate flask (Justi Miracleglask Intro Kit-FRP, Justi Products, American Tooth Industries) using the stainless steel sprue former supplied with the flask. The flasks were placed in a 600 W domestic microwave oven on full power for one minute to soften the wax, which was then removed and tin foil substitute was applied. The flasks were closed and injected with Shera-Med NW 2000 (Dental-Werkstoffe, Lemförde, Germany) PMMA dough mixed according to the manufacturer's instruction and the pressure-retaining device was fitted. The flasks were processed in a 600 W microwave oven on full power for 3 min, cooled on the bench for 0.5 h and placed in cold water for 0.5 h. The acrylic specimens were then retrieved, finished and polished.

Group 4 specimens were made with Shera-Med NW 2000 (PMMA) of the same dimensions as above, reinforced with glass fibers which were 5-10 μm thick and were cut to 2.5 mm lengths. The cut fibers were soaked in monomer for 10 min to allow for better bonding with the acrylic fibre. The fibers were removed from the monomer and the excess liquid was allowed to dry. The resin and fibers (2 % by weight) were mixed thoroughly to disperse the fibers. After reaching the dough stage, the mixture was kneaded and packed into the prepared mould. The specimens were polymerized and recovered in the same manner as group 3.

Preparing samples for the chemical shift measurements: After polymerization of the all specimens, all specimens were prepared in the dusty form by granulating the materials. The small portion of the solid additives was removed by centrifugation.

1 mL of a mixture of H_2O (80 %) and D_2O (20 %) was also prepared for each sample. The $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture was poured into an NMR tube with 5 mm in O.D. Then 5 mg of the material was successively added to the mixture and then stirred gently after each addition by using a very thin steel rod. The stirring was maintained until the homogeneous sample was obtained (Fig. 1). The same procedure was used for the preparation of each sample.

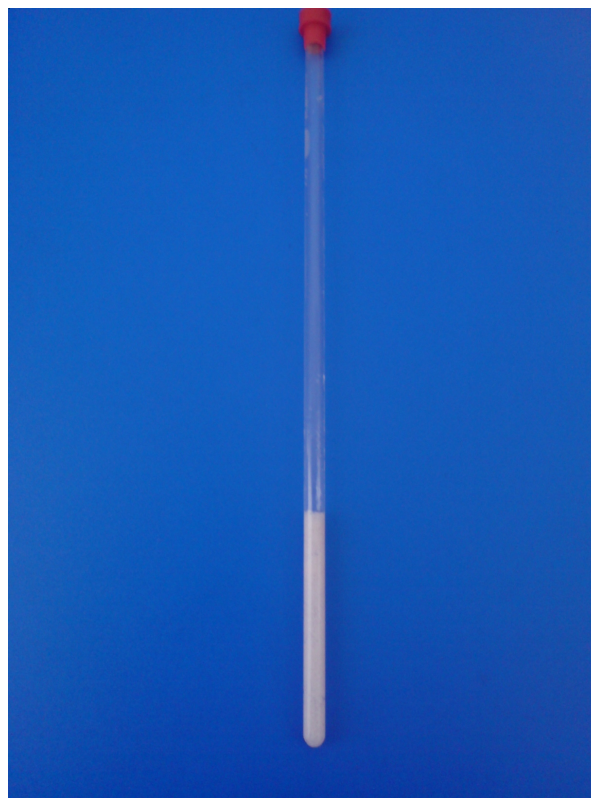


Fig. 1. View of the specimens

The water proton signals in samples were obtained by a Bruker NMR spectrometer operating at 400 MHz. The chemical shifts of signals were measured by using the pointer on the top of each signal. The measurements have been repeated for 6 days. During the measurements, a special attention was paid to the shim adjustment and also phase and baseline corrections. The experimental errors for chemical shifts measured in the

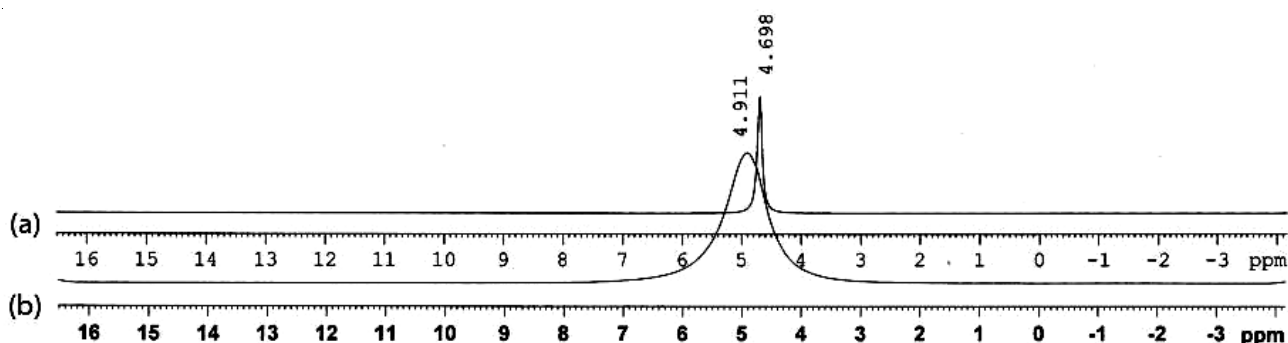


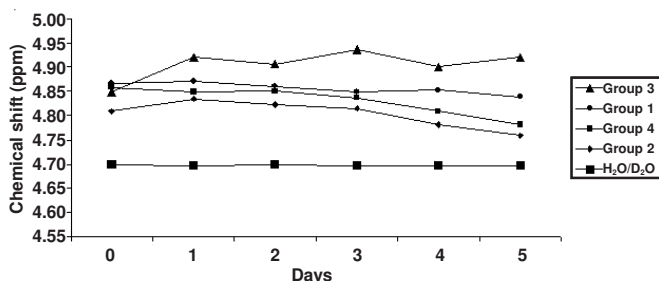
Fig. 2. Chemical shift of pure mixture

pure mixture, based on ten successive measurements, were 0.0001 ppm.

RESULTS AND DISCUSSION

For demonstrative purposes, the chemical shifts of the pure mixture and a representative sample were shown in Fig. 2. The chemical shift of pure mixture is 4.698 ppm, while those of the samples have different values. Fig. 2 indicates that the chemical shift of the dental sample is different than that of pure mixture (80 % D₂O and 20 % H₂O).

The chemical shifts of peaks *versus* days were shown in Fig. 3 for each group. It is clearly seen that the chemical shifts of all groups are higher than pure mixture. The chemical shifts of group 3 are higher than that of group 4, while the chemical shift of group 1 is higher than that of group 2. Furthermore, the chemical shifts of material polymerized by microwave are higher than those polymerized by injection (group 3 > group 1, and group 4 > group 2).

Fig. 3. Chemical shifts of peaks *versus* days for each group

The interaction of of methacrylate molecule with other materials and the chemical bonding to hydroxyapatite by phosphoric acid esters were studied by chemical shift^{14,15}. The mechanisms of methacrylate-induced toxicity and NMR-analysis of monomers in restorative resins were also studied by high resolution NMR^{16,17}. The chemical shift yielded useful information for each case. Such differences in chemical shifts reported by those studies indicate that water is absorbed by methacrylate molecules. Hence the present study is consistent with the previous investigations.

On the other hand, the environmental change of water can be followed through spectrum of proton signals of dental samples¹⁸⁻²⁰. The comparison of the line widths of signals given in Fig. 2 shows that the line width is broadened in the presence of dental material. Since the line broadening is caused by water

absorption, the line widths give in Fig. 2 confirms the absorption of water by the material.

In the presence of two different environments for water such as free water and water in material, the chemical shifts of free and bound water can be denoted by δ_f and δ_b , respectively. If there is a fast water exchange between these two environments, the observed chemical shift is the weighted average of those characteristic of the individual environments

$$\delta_{\text{obs}} = \left(\frac{N_f}{N} \right) \delta_f + \left(\frac{N_b}{N} \right) \delta_b \quad (1)$$

where N_f , N_b and N denotes the number of free water molecules, absorbed water molecules and total water molecules, respectively¹³. Accordingly, a single resonance line is observed for fast exchanging water. The single water signal shown in Fig. 2 is a good indicator for the fast exchange of water between free water and water absorbed by the current materials.

The differences between chemical shifts of the dental materials and pure H₂O/D₂O mixture are directly related to eqn. 1. When water is not absorbed, $N_b = 0$, $N_f = N$ and $\delta_{\text{obs}} = \delta_f$. In such case, signals obtained from materials would give a chemical shift equal to that of mixture. However, the shifts reported in Table-1 shows that N_b is not zero. This means that some water molecules are absorbed by materials through chemical exchange of water between free and bound phases. In fact, ¹H NMR studies on water in methacrylate hydrogels has showed that the water in these hydrogels was classified into three states *i.e.*, free, intermediate and bound states¹⁸. The mobility of water in poly (methyl methacrylate) is several orders of magnitude higher than that in poly (hydroxyethyl methacrylate). In addition, dental impression alginate materials were studied by NMR in terms of bound and unbound water¹⁹. Their results were suggested to open a way to formulate alginate impression materials more suitable for precise fabrication of dental prostheses. The analysis of the present data, in terms of water classes, is the consistent with those studies.

The differences in the chemical shifts (Fig. 3), are dependent on the second term in eqn. 1. The small N_b means small amount of absorbed water and also small difference in chemical shift of dental material relative to that of pure mixture. Higher N_b expresses higher amount of absorbed water and also higher difference in chemical shift of dental material relative to that of pure mixture. Accordingly, the higher chemical shifts of group 1 and group 3 indicate that the water absorption of each of these groups without fiber is clearly higher than that of

relevant group 2 and group 4 materials with fiber (group 1 > group 2, and group 3 > group 4). The data in Table-2 also shows that water absorption of materials polymerized by microwave is higher than similar material polymerized by injection (group 4 > group 2, and group 3 > group 1).

TABLE-2
AVERAGE VALUES WITH STANDARD DEVIATIONS OF
CHEMICAL SHIFT DATA (ppm)

Groups	Chemical shift (ppm)
Group 1	4.8562 ± 0.0116
Group 2	4.8039 ± 0.0284
Group 3	4.9054 ± 0.0310
Group 4	4.833 ± 0.0215

Conclusion

In this study, water absorption was significantly correlated with their NMR chemical shifts. Present data suggest that the material with fiber absorbs less water. The data also suggest that material polymerized by injection absorbs less water than material polymerized by microwave. The less absorption of water by dental materials with fiber (group 2 and group 4) implies that fiber prevents absorption of water by material. This is consistent with the data of group 1 and group 3 which are not fortified by fiber. The absence of fiber causes more absorption of water by dental material. Furthermore, comparison of heat cured acrylic resin and microwave cured acrylic

resin data shows that the materials polymerized by heat cured absorb less water relative to those polymerized by microwave.

REFERENCES

1. K. Hiromori, K. Fujii and K. Inoue, *J. Oral Rehabil.*, **27**, 522 (2000).
2. D.M. Wong, L.Y. Cheng, T.W. Chow and R.K. Clark, *J. Prosthet Dent.*, **81**, 300 (1999).
3. J.L. Garcia-Fierro and J.V. Aleman, *Macromolecules*, **15**, 1145 (1982).
4. S.H. Tuna, F. Keyf, H.O. Gümüs and C. Uzun, *Eur. J. Dent.*, **2**, 191 (2008).
5. A.L. Cucci, C.E. Vergani, E.T. Giampaolo and M.C. Afonso, *J. Prosthet Dent.*, **80**, 434 (1998).
6. A.S. Hargreaves, *J. Dent.*, **6**, 342 (1978).
7. B. Ristic and L. Carr, *J. Prosthet Dent.*, **58**, 689 (1987).
8. S. Kalachandra and D.T. Turner, *Dent. Mater.*, **5**, 161 (1989).
9. M.P. Patel and M. Braden, *Biomaterials*, **12**, 653 (1991).
10. M.J. Barsby, *J. Dent.*, **20**, 240 (1992).
11. ISO 1567:1999, Denture Base Polymers.
12. V.M. Miettinen, P.K. Vallittu and D.T. Docent, *J. Prosthet Dent.*, **77**, 531 (1997).
13. O. Jardetzky and G.C.K. Roberts. NMR in Molecular Biology, Academic Press, New York, p. 115 (1981).
14. S. Fujisawa, M. Ishihara and Y. Kadoma, *J. Liposome Res.*, **15**, 167 (2005).
15. B. Fu, X. Sun, W. Qian, Y. Shen, R. Chen and M. Hannig, *Biomaterials*, **26**, 5104 (2005).
16. I. Mariko and W.A. Fujisa, *Dental Mater. J.*, **28**, 113 (2009).
17. E. Asmussen, *Acta Odontolog. Scand.*, **33**, 129 (1975).
18. A.Y. Nosaka, K. Ishikiryama, M. Todoki and H. Tanzawa, *J. Appl. Polym. Sci.*, **39**, 2443 (1990).
19. C.M. Fellows and G.A. Thomas, *Dental Mater.*, **25**, 486 (2009).
20. S. Kawaguchi and M.A. Winnik, *Macromolecules*, **29**, 4465 (1996).