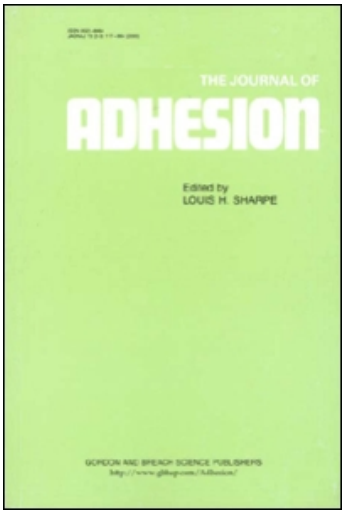

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Chemical Reactions Between Dentin and Bonding Agents

M. Di Renzo[a]; T. H. Ellis[a]; A. Domingue[b]; L. Bertrand[b]; E. Sacher[b]; I. Stangel[c]
[a] Département de chimie, Université de Montréal, Québec, Canada [b] Département de génie physique, École Polytechnique, Québec, Canada [c] Faculty of dentistry, McGill University, Québec, Canada

To cite this Article Renzo, M. Di , Ellis, T. H. , Domingue, A. , Bertrand, L. , Sacher, E. and Stangel, I.(1994) 'Chemical Reactions Between Dentin and Bonding Agents', The Journal of Adhesion, 47: 1, 115 — 121
To link to this Article: DOI: 10.1080/00218469408027093
URL: http://dx.doi.org/10.1080/00218469408027093

J. Adhesion, 1994, Vol. 47, pp. 115–121
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Chemical Reactions Between Dentin and Bonding Agents*

M. DI RENZO and T. H. ELLIS

Department de chimie, Université de Montréal, Montréal, Québec H3C 3J7, Canada

A. DOMINGUE, L. BERTRAND and E. SACHER**

Department de génie physique, École Polytechnique, Montréal, Québec H3C 3A7, Canada

I. STANGEL

Faculty of dentistry, McGill University, Montréal, Québec H3A 1A4, Canada

(Received November 27, 1992; in final form May 5, 1993)

The possible interaction between dentin and a proprietary dentin bonding agent (DBA), Gluma, was studied by Phase Photoacoustic FTIR. The determination of the existence and nature of a chemical bond between the DBA and the substrate can be of great importance in explaining the performance of these agents. Human dentin was treated by solutions of 2-hydroxyethyl methacrylate (HEMA), glutaraldehyde and a combination of both (Gluma Primer). Spectra of dentin samples treated with 35% and 100% HEMA as well as Gluma Primer show loss of both the hydroxyl (O—H stretch) and methylene (CH_2 stretches) peaks from HEMA while other peaks are retained, even after thorough washing. This indicates a reaction between HEMA and the collagenous fraction of dentin.

KEY WORDS dentin adhesives; vibrational spectroscopy; photoacoustic spectroscopy; HEMA (hydroxyethyl methacrylate); transesterification; chemical bonding.

INTRODUCTION

Achieving a strong and durable bond to dentin through the use of dentin bonding agents (DBA) is of great importance in dental restorative techniques. In recent years, there has been much debate as to how such a bond may be obtained. Bonding is believed to occur through either mechanical or chemical interaction, or possibly a combination of both.[1,2,3,4,5] Although bonding between dentin and a bonding agent is sometimes suggested to be of a chemical nature, for which several reactions have been proposed,[6,7] there is little direct proof of its existence.

Chemical bonding to dentin is believed to occur from a reaction between the adhesive and functional groups present in collagen (carboxylate, hydroxyl, amido or

*Presented at the Sixteenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 21–26, 1993.

**Corresponding author.

amino groups) and/or by complexation with Ca^{2+} ions from hydroxyapatite (HAP). In the case of the Gluma system, it has been suggested that a first reaction occurs between glutaraldehyde and amino groups present in collagen, followed by the reaction of HEMA with the collagen-bonded glutaraldehyde.[7,8] Others have suggested that the effect of glutaraldehyde may not be as obvious.[9] No reaction is suggested to take place between the bonding agent and HAP.

The optical technique best suited for the study of chemical structures is infrared (IR) spectroscopy. It measures characteristic vibrations of bonds present in the chemical groups of molecules. This study uses Phase Photoacoustic FTIR (PHAS-FTIR/PAS),[10] a surface sensitive IR technique, to probe the effect of the DBA Gluma and its components (glutaraldehyde, HEMA) on dentin and calcium hydroxyapatite. PHAS-FTIR/PAS is a photoacoustic spectroscopic technique adapted to surface studies based on the measurement of pressure changes in a coupling gas above the sample. These pressure changes are caused by heat released by the sample upon absorption of IR radiation. Since only radiation absorbed close to the surface reaches the coupling gas, it is possible to obtain spectra containing the surface signal. This technique offers two main advantages; the first is that spectra of normally-opaque samples (such as dentin) can be obtained. The second is that PAS is a null technique, meaning no absorption, no signal; this permits minor peaks and variations to be more easily seen. The variant of the photoacoustic technique used in this experiment utilizes phase separation, allowing us to overcome some photoacoustic artifacts often found in heterogeneous samples such as dentin. Previous studies using a similar technique have either failed to prove the existence of any chemical bonds in the systems used[4] or have shown that chemical bonding is a possibility.[11,12]

In this study, PHAS-FTIR/PAS is used to follow specific changes in the chemistry of dentin and HAP following the application of Gluma and its individual chemical components. The ultimate goal is to elicit any reaction (or reactions) between dentin and bonding agent. Such an understanding will be helpful in directing future research aimed at improving the performance of these agents.

EXPERIMENTAL

The materials used were the following: 2-hydroxyethyl methacrylate was obtained from Sigma Chemicals (St. Louis, MO, USA); glutaraldehyde (25%) was obtained from the Aldrich Chemical Company (Milwaukee, WI, USA); calcium hydroxyapatite was supplied by Calcitek (San Diego, CA, USA); dentin samples were obtained from freshly-extracted human molars, sectioned parallel to the occlusal surface to obtain dentin disks. The disks were stored in a desiccator for no more than two weeks. Commercial Gluma was obtained from Bayer (Dormagen, Germany).

Dentin was treated by dipping the disks in freshly-prepared solutions of either 5% glutaraldehyde, 35% HEMA or 5% glutaraldehyde and 35% HEMA (Gluma Primer) in deionized water for 10 minutes, following which they were thoroughly rinsed and dried under an air jet. HAP powder was added to test tubes filled with solutions prepared as mentioned above and occasionally stirred in a thermostated

bath at 37.5°C for 10 minutes, filtered, thoroughly washed in deionized water and dried under vacuum for 2 days. A standard was prepared using the same procedure but by replacing the solutions with deionized water.

Spectra were obtained on a Bomem DA-3 FTIR spectrometer, in the range of 750 to 4000 cm^{-1} at a resolution of 8 cm^{-1}. The photoacoustic cell was specially designed to increase the ease of sample mounting and reduce thermal loss. Helium was used as the coupling gas. A high sensitivity miniaturized Knowles EK-3103 microphone was used to detect the pressure changes. To increase S/N, one thousand scans were co-added for dentin and four hundred for HAP, at a mirror speed of 0.1 cm/sec. Unless otherwise noted, all spectra have their standard already subtracted.

RESULTS

A spectrum of Gluma Primer (GP) solution can be found in Figure 1. It was obtained by depositing and partially drying the solution on a metal support. Peaks can be seen at 1165, 1298, 1319, 1720 and ~2950 cm^{-1} as well as a broad band centered around 3450 cm^{-1}. The broad band is due to hydrogen bonding from the water and hydroxyl groups in HEMA present in the solution; the other peaks are commonly the most intense peaks found on spectra of pure HEMA.[13] By comparison, the treated dentin spectrum (Figure 2) has peaks only at 1170, 1298, 1320 and 1720 cm^{-1}. There is no evidence of the bands at ~2950 cm^{-1} (CH_2 symmetric and asymmetric stretches) nor of the hydroxyl group (~3500 cm^{-1}, the O—H stretching vibration), hydrogen bonded or not, usually found for HEMA. Note that the peak that

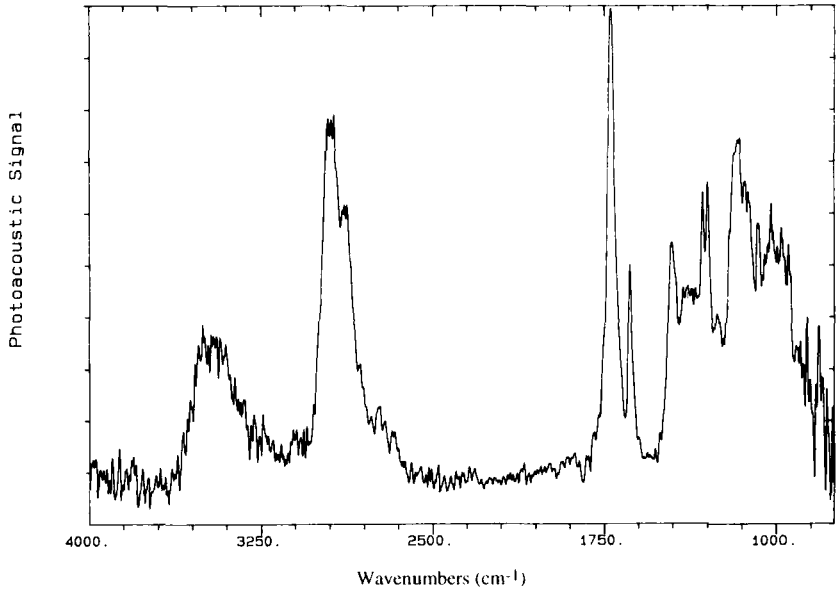

FIGURE 1 Spectrum of Gluma Primer.

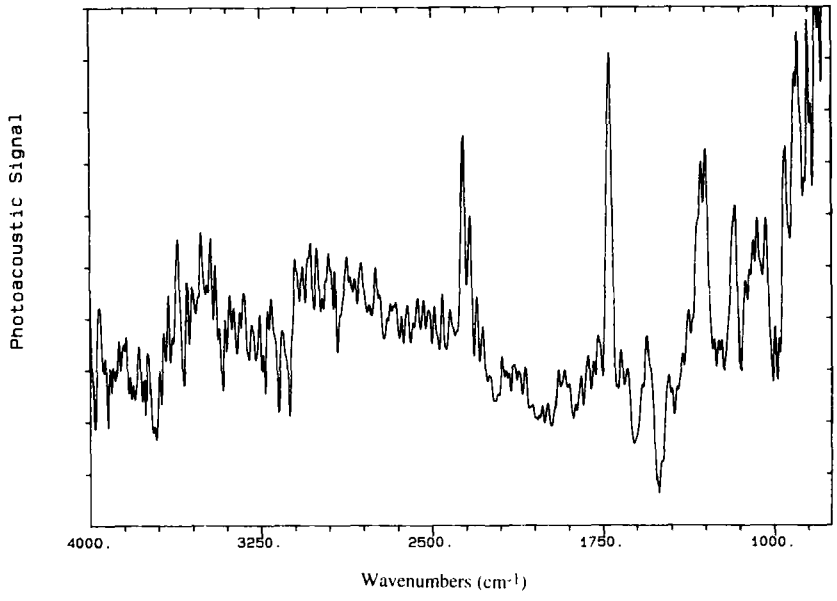

FIGURE 2 Subtraction spectrum of dentin treated with Gluma Primer.

appears at ~2300 cm^{-1} in many of the spectra is due to gas-phase CO_2 stretching; since it is difficult to remove all the air from the photoacoustic cell, this peak is often present.

Treating dentin with either a 35% solution of HEMA in water or 100% HEMA results in spectra (Figures 3 and 4, respectively) having peaks at ~1170, ~1300 and ~1720 cm^{-1}. These characteristic peaks match those found above; yet again, there is no evidence of either the CH_2 or O—H stretching peaks.

After subtraction of the apatite standard (clean and untreated HAP), the calcium hydroxyapatite spectrum resulted in a flat, clean baseline. HAP treatments showed neither new peak formation nor loss.

Dentin samples treated with glutaraldehyde showed no significant changes in chemical structure except for a very weak peak at around 1700 cm^{-1}. As this peak could not be reproduced in all experiments, it may be a contaminant left from the washing.

DISCUSSION

Vibrational spectroscopy is a useful tool to help understand the interaction between dentin and DBA. If any significant modification to either DBA or substrate occurs, certain vibrational peaks should be modified; peaks may have shifted in position, they may disappear and/or new peaks may be formed. Any one of these modifications indicates a chemical change in the region observed. These modifications may help us determine the reaction that is occurring.

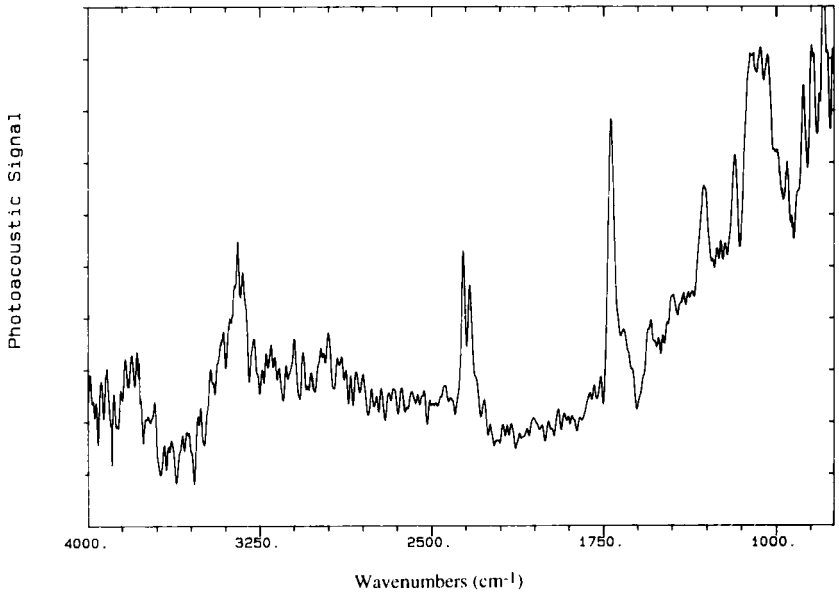

FIGURE 3 Subtraction spectrum of dentin treated with 35% HEMA.

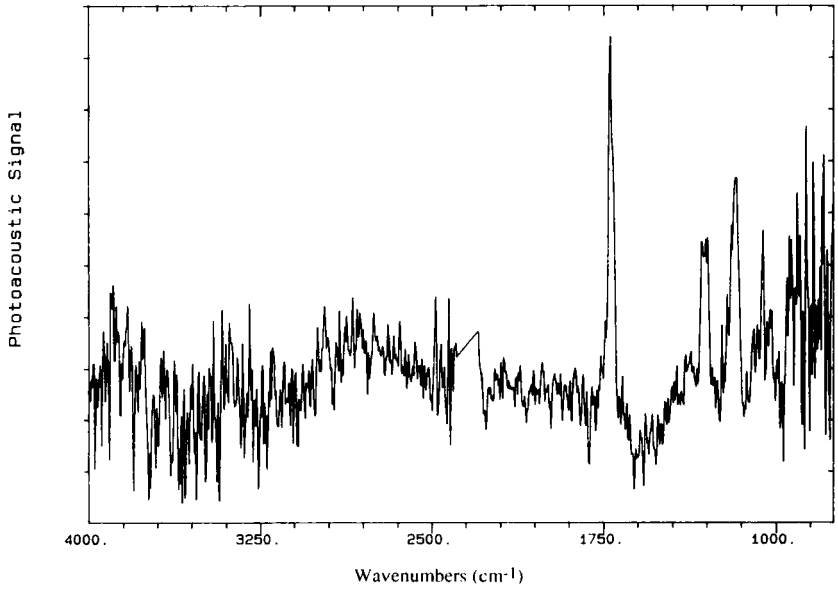

FIGURE 4 Subtraction spectrum of dentin treated with 100% HEMA.

As previously noted, all the peaks found in the spectra of dentin treated with either the Gluma Primer or a HEMA solution are commonly found in the spectrum of pure HEMA, with the noted exceptions being the region around 2950 cm^{-1} and the broad band centered at 3450 cm^{-1} (found only in the Gluma Primer solution itself). As can be seen from these results, the peaks situated at ~1170, ~1300 and ~1720 cm^{-1} are present in pure hydroxyethyl methacrylate, thus indicating that at least some fraction of the molecule is present at or near the interface. These peaks are consistent with the ones commonly assigned to esters with double bonds, such as methacrylates. The strong peak close to 1720 cm^{-1} is assigned to the C=O stretching frequency, the peak at 1170 cm^{-1} is assigned to the C—O stretching of the ester group and, finally the peak close to 1300 cm^{-1}, which can often be resolved into a doublet (Figures 1, 2 and 4), is assigned to a $C{=}CH_2$ rocking vibration (1300 cm^{-1}) and a $C{=}CH_2$ deformation (1325 cm^{-1}).[14]

The disappearance of the hydroxyl group of HEMA (~3500 cm^{-1}) as well as the bands around 2950 cm^{-1} ($R\text{-}CH_2\text{-}R'$, symmetric and asymmetric stretching vibrations) indicates that a reaction has occurred at the ester linkage. The latter reaction may involve a trans-esterification and/or -amidization with groups present in the collagen. This evidence clearly indicates a significant change in the chemical structure of HEMA upon contact with collagen.

Given the similarity between spectra of samples treated with HEMA and those treated with Gluma Primer, the effect of glutaraldehyde seems unclear. The only effect detected at very high magnification in some spectra, following glutaraldehyde solution treatment, was a weak peak at 1700 cm^{-1} and is probably a contaminant left from the washing. Our experiments have failed to detect a definite presence of glutaraldehyde; therefore, we are unable to conclude if its presence is necessary for a reaction to occur. The lack of any effect of glutaraldehyde has previously been reported.[9]

As originally thought, the Gluma system leaves HAP untouched, as no new peaks were detected on any of the treatments. This is to be expected, as none of the components of Gluma Primer have any affinity to form complexes with calcium hydroxyapatite.

CONCLUSION

Evidence shown in this study indicates that 2-hydroxyethyl methacrylate is capable of chemically bonding to the collagenous fraction of dentin. This bond does not depend on the presence of glutaraldehyde. This latter component of the Gluma Primer solution has an effect which is unknown or undetectable with respect to the bond created between dentin and DBA. Calcium hydroxyapatite is untouched by Gluma, as expected.

Acknowledgments

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada and the Fonds pour la Formation des Chercheurs et à l'Aide à la Recherche du Québec for funding. They wish to thank Calcitek for the gift of high purity calcium hydroxyapatite.

References

1. E. Asmussen and E. C. Munksgaard, *Internat. Dent. J.* **35,** 160 (1985).
2. X. Y. Yu, G. Wieczkowski, E. L. Davis and R. B. Joynt, *Quintessence Int.* **21,** 989 (1990).
3. R. L. Erickson, *Am. J. Dent.* **2,** 117 (1989).
4. P. Spencer, T. Byerley, L. Marshall, D. Eick and J. Witt, *J. Dent. Res.* **70,** 458 (1991).
5. N. Nakabayashi, K. Kojima and E. Masuhara, *J. Biomed. Mater. Res.* **16,** 265 (1982).
6. E. Asmussen and E. C. Munksgaard, *Internat. Dent. J.* **38,** 97 (1988).
7. F. Fava, C. Prati, L. Marchetti and G. Montanari, *Ann. Chim. (Rome)* **80,** 487 (1990).
8. E. Asmussen and E. C. Munksgaard, in *Posterior Composite Dental Restorative Materials,* G. Vanherle and D. Smith, Eds. (3M Company, St. Paul, MN, 1985), pp. 217–229.
9. G. Eliades, G. Palaghias and G. Vougiouklakis, *Dent. Mater.* **6,** 208 (1990).
10. L. Bertrand, *Appl. Spectrosc.* **11,** 10 (1988).
11. I. Stangel, E. Ostro, A. Domingue, E. Sacher and L. Bertrand, in *Proceedings from the First International Conference on Polymer-Solid Interfaces,* J. J. Pireaux, P. Bertrand and J. L. Bredas, Eds. (Institute of Physics Publishing, Bristol, 1992), pp. 157–167.
12. C. Kamel, I. Stangel, A. Domingue, E. Sacher and L. Bertrand, *J. Dent. Res.* **71,** 666 (1992).
13. C. Pouchert, *Aldrich Library of Infrared Spectra,* 3rd. edit. (Aldrich, Milwaukee, 1981), p. 390.
14. N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy,* 3rd. edit. (Academic Press, San Diego, 1990), pp. 300–306.