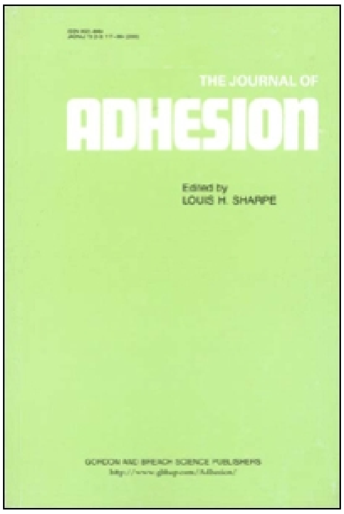

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Influence of Roughness on Wetting and Adhesion in a Dental Adhesive System

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Influence of Roughness on Wetting and Adhesion in a Dental Adhesive System

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In this investigation the fracture surface between bovine dentine and bovine enamel and a dental cement was observed using the scanning electron microscope at magnifications up to 10,000 ×. The results indicated that the topography of the adherend plays an important role in the formation of an adhesive bond and in the fracture pattern of an adhesive joint, even when cohesive failure is involved.

INTRODUCTION

In many cases, two materials will adhere because of secondary or van der Waal's attractive forces acting between the atoms, ions, molecules or molecular segments in the two surfaces. Since these secondary forces act over very small distances only (see, e.g. Good[1]), the two surfaces must be brought closely together for these forces to be effective. For example, if two solids, A and B, have absolutely planar surfaces, smooth on an atomic scale which were brought together in a perfect vacuum, there would be a very considerable force of adhesion, particularly if the interfacial free energy were low[2]. However, real surfaces differ from these ideal conditions in that they are rough and this may contribute to a greatly decreased real area of contact. Thus, to get A and B to make a strong adhesive bond, it is necessary to increase the real area of contact, i.e. one material must be made to conform as much as possible to the surface topography of the other.

This implies, in a practical sense, that one of the materials should be fluid when placed in contact with the other. Thus, the question of the wettability of the solid surface arises. We use wettability rather broadly as being the manifestation of static and dynamic contact angle effects.[3] In the process of wetting there may be contact angles operative which are different from static ones and these are designated as dynamic contact angles. They determine rate effects via their influence on the Laplace pressure.[4] They may eventually bring the system to a metastable or, at least, stationary state which will, from the point of view of adhesion, be less favorable than the true equilibrium configuration or the metastable state reached when dynamic effects are not present.[5]

While a true equilibrium contact angle will be observed only on a smooth, homogeneous solid surface, the metastable contact angles observed on heterogeneous, but smooth solid surfaces may have a thermodynamic significance[5] and may be related to interfacial free energies, similar to true equilibrium contact angles. Thus, contact angles may also be used as a measure for interfacial free energies, which decrease with decreasing contact angle.[2,6] The possible relevance of interfacial free energies appears to be rather obvious. For example, if there are two adhesive systems which are identical except for the fact that the interfacial free energy in one case is zero, but is finite in the other case, the overall free energy of the system with zero interfacial free energy is lower and the adhesive joint should be stronger.

On a rough surface, the liquid may do a great deal of bridging, trap pockets of air, and achieve little penetration into the depressions in the surface of the adherend, thus creating what is termed a composite surface.[7,8] The question of whether static or dynamic contact angles are operative in the formation of the composite surface, although clearly important, is not discussed in this paper. The enclosed air pockets give rise to stress concentrations at the interface. In addition to possible implications with respect to interfacial free energies, the effect of having a spontaneous spreading situation or a surface which has been optimally wetted is twofold: (1) the real area of contact is increased, and (2) the stress concentration at the interface is minimized. Therefore, it should be clear that the microtopography of the solid surface is one of the major variables influencing wetting and adhesion.[7,8,12,16–21]

The necessity of good wetting in order to establish good adhesion is agreed upon by many investigators,[2,3,9–13] at least with respect to many of the aspects of wetting explained above, and at least as far as the formation of the adhesive joint is concerned. It has been argued,[14] however, that a correlation between adhesive strength and wetting is not to be expected, since a truly adhesive failure very seldom occurs, at least not with good adhesive joints. It was argued that a phenomenon such as wetting, which is a function of both the adhesive and adherend phases, should not be related to cohesive failure, which occurs in only one of the two phases.[14] On the other hand, results have been reported[2,6,15] which indicated a correlation between wetting and strength of adhesion for low energy solids.

The present investigation attempts to indicate a path along which this apparent discrepancy may be resolved. It is the purpose of this investigation to contribute to the clarification of the arguments discussed above by investigating directly the surfaces exposed after fracture of a dental adhesive joint, by means of scanning electron microscopy.[22,23] The intent of the investigation is to shed some light on the question of whether the topography of the adherend plays a role only in the formation of an adhesive bond, or whether it also influences the strength of an adhesive joint.

EXPERIMENTAL

A dental cement† placed on bovine dentine and enamel under controlled conditions was the system used in this investigation. This cement† reportedly[24] chelates with the inorganic phase of tooth structure in the presence of water and an adhesive bond is formed.

Samples of bovine enamel and dentine were surfaced flat through 400 grit with SiC paper under wet conditions. The prepared tooth surface was placed in a specially designed jig[25] used to minimize stress concentrations during sample preparation. A teflon disk, one inch in diameter and three-tenth inch thick, have a 5 mm. diameter hole centrally drilled, was used as a die to limit the spread of the cement on the substrate surface. The cement was mixed according to the manufacturer's directions and packed into the teflon mold onto the tooth surface. A machine screw was placed precisely 1 mm. above the substrate surface in the cement to act as an attachment for tensile testing and the specimen was stored under wet conditions at 37°C for 24 hours. The adhesive bond was then tested in tension using an Instron Testing Machine operated at a crosshead speed of 0.05 cm/min. The procedure described by the Subcommittee on Standard Test Methods for Direct Filling Resins, I.A.D.R.[25] for preparation and testing of the specimens was followed. Five samples using bovine enamel and five samples using bovine dentine were tested. The specimens were maintained in water at 23°C after tensile testing to minimize dimensional changes of the cement

† Duralon, manufactured by ESPE GmbH (Seefeld/Oberbay, W. Germany), Liquid Lot No. 105 and Powder Lot No. 437.

during storage and then vacuum coated with a 200–400 Å layer of Au–Pd immediately before being placed in the scanning electron microscope. A Cambridge Stereoscan scanning electron microscope operated at 10 kV and a specimen stage tilt of 45° was employed to observe the fractured surfaces up to 10,000 × magnification.

RESULTS AND DISCUSSION

A fractured interface is shown in Figure 1 at 20 ×, 100 × and 500 × ; the adherend in this case is bovine dentine. Approximately half of the cement has been completely removed from the dentine with a rather thick outer ring of cement remaining, suggesting a ductile fracture pattern predominated.[26] This fracture pattern was typical of most of the dentine and enamel specimens

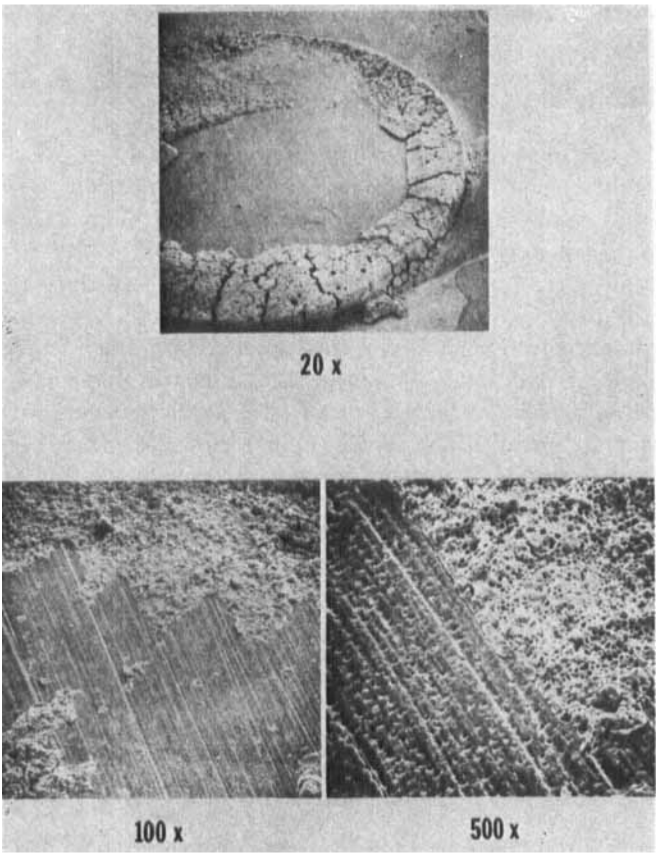

FIGURE 1 Adhesive interface between bovine dentine and cement.

tested, with generally more cement remaining on the enamel samples than on the dentine samples. This may be related to the larger amount of inorganic material in enamel than in dentine which could have caused the chelation reaction to be more extensive, thus producing a more complete bonding. An interpretation of the fracture pattern (Figure 1, 20 ×) is that failure started somewhere in the inside of the specimen, probably at the adhesive-dentine interface, and propagated outwards. Near the edge of the sample, the failure locus moved away from the interface and into the adhesive. This interpretation seems reasonable, especially since the fracture joint appeared to have a cup and cone configuration, indicating that ductile fracture predominated. In such cases, the crack nucleates near the center of the specimen and proceeds outward.[26]

The scratches produced during preparation are clearly shown at 100 × magnification and the dentinal tubules appearing as small holes are visible at 500 ×. Of particular interest is the region shown at 100 ×. In three separate areas, the fracture pattern appears to follow closely the scratches in the substrate left during preparation. This point is more clearly illustrated at 500 ×, where the center area has been magnified.

In Figure 2, scanning electron micrographs of the center area which was shown in Figure 1 are shown up to 5000 ×. Filler particles of zinc oxide[24] remain on the surface of the cement and a large particle is clearly visible at 1000 × and 2000 × in the upper-right corner. The mass of adhesive was porous or spongy throughout, with void spaces in the range of 0.2 to 15 μm. across, as may be seen in all the micrographs in this figure. The void spaces are of two classes, those that extended down to the dentine surface (see Figure 4) and those that did not. The bubbles that were entirely in the cement probably were formed by entrapment of air during the mixing of the cement. Those that extended down to the dentine most likely were formed by entrapment of air during the application of the cement onto the tooth surface; they were generally larger than those entrapped during mixing. Two large voids which appear to be a cluster of two or three bubbles are shown at 2000 × and 5000 × in Figure 2. They may be air pockets; however, due to their irregular shape, they are more likely depressions left after filler particles have been removed during testing. The topographical appearance of the dentine after surface preparation and adhesion testing is also shown clearly in this series of micrographs.

A different region of this same area is shown in Figure 3. Again filler particles, air bubbles and the topography of the dentine are clearly shown. Of special interest is the fracture pattern of the adhesive bond between the cement and the dentine. The gap between the cement and the dentine, a space about 0.5 μm. wide running diagonally in the photographs and parallel to ridges in the dentine, was probably formed along after the fracture occurred.

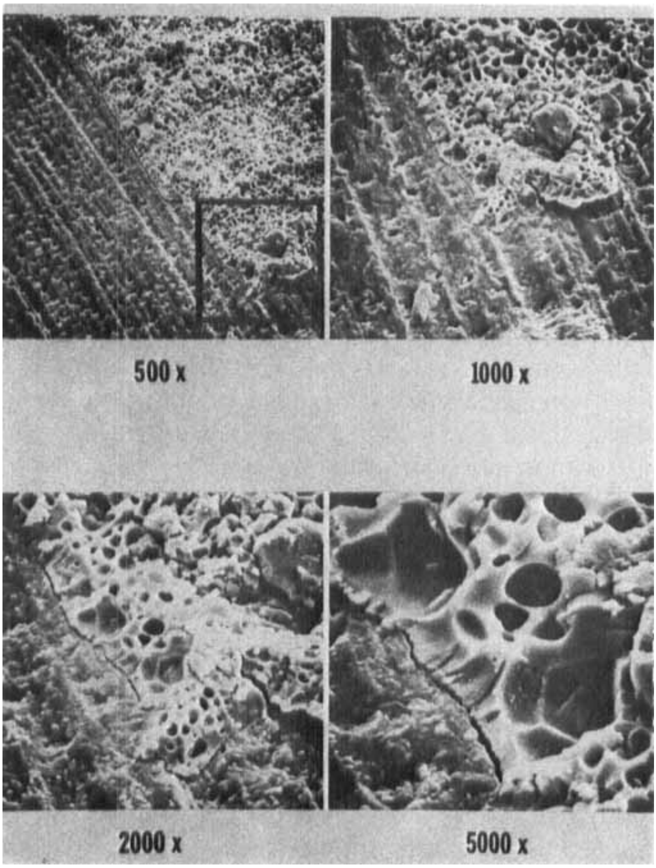

FIGURE 2 Adhesive interface between bovine dentine and cement.

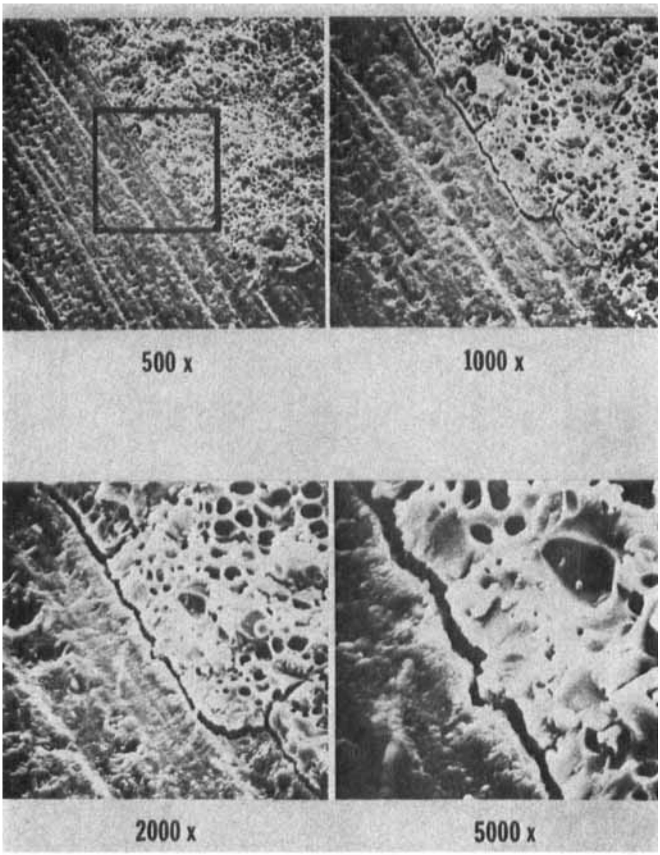

FIGURE 3 Adhesive interface between bovine dentine and cement.

It most likely developed during the drying and subsequent shrinkage of the cement during metal coating. The fracture surface itself appears to have propagated from lower left to upper right, following the dentine surface. At the top of one of the ridges it started into the cement, and thereafter continued as a cohesive failure. It is well known from stress analysis that a sharp edge, such as the tip of this ridge, will be a region of stress concentration, and will consequently influence the fracture pattern. In this case, the topography of the dentine substrate obviously influenced the fracture pattern to a considerable extent. Also of interest is the fact that the dentinal tubules act as capillaries during the wetting process, illustrated by the fact that the cement has penetrated into the tubules as shown at 2000 × and 5000 ×. Therefore, the tubules also influenced the wetting and subsequent fracture pattern considerably.

Another specimen of a fractured surface of bovine dentine and cement is shown in Figure 4. This specimen has been cleaved through the tooth structure perpendicular to the plane of the adhesive bond. The cleavage is shown in the lower left corners of the photomicrographs at 500 × and 1000 ×. In this area dentinal tubules and the structure of the dentine can be clearly observed.

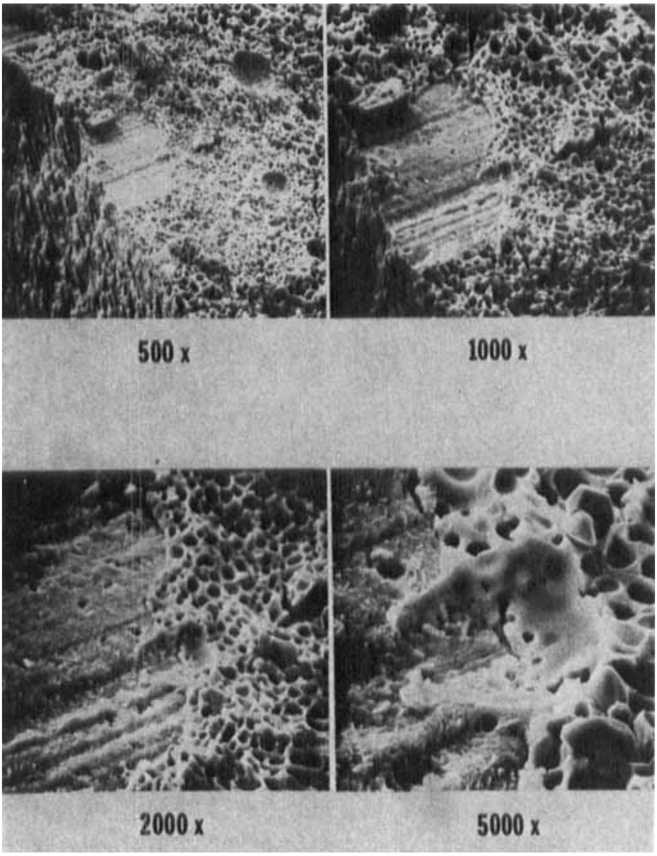

FIGURE 4 Adhesive interface between bovine dentine and cement.

A few rather large air pockets are present in the cement and one of these is visible at the region between the dentine and cement. This bubble has been entrapped at a large groove in the substrate and it can be seen that the cement did not wet the dentine completely in this area. This is shown at 2000 × and 5000 ×. These photomicrographs also illustrate the fact that the topography of the dentine affected the wetting process itself, as well as the subsequent adhesive bond.

Two different areas of fracture of a specimen of cement on enamel are shown in Figure 5. The enamel surface outside of the test area is shown in the upper right corner of the micrographs. There are no tubules present in this structure; however, the grooves produced during surface preparation are present. In the area shown, the cement cohesively fractured very near the enamel surface, unlike the fracture surfaces with dentine where the cement cohesively failed farther from the dentine substrate. A thick ridge of cement remained around the outer circumference, which runs diagonally through the micrographs. It is quite clear that small air pockets in the cement tended to "line-up" along the grooves produced during surfacing.

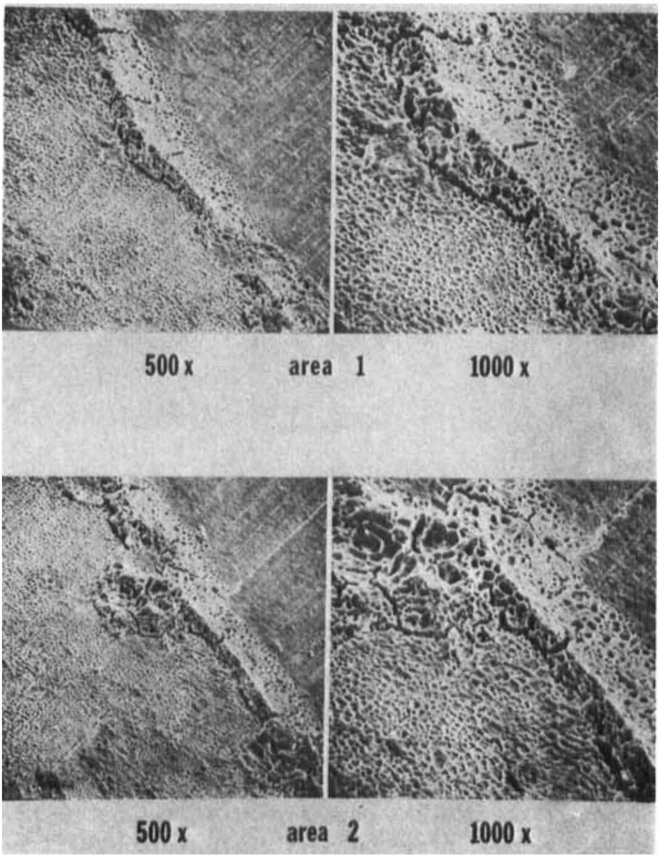

FIGURE 5 Adhesive interface between bovine enamel and cement. Note concentration of air pockets along grooves.

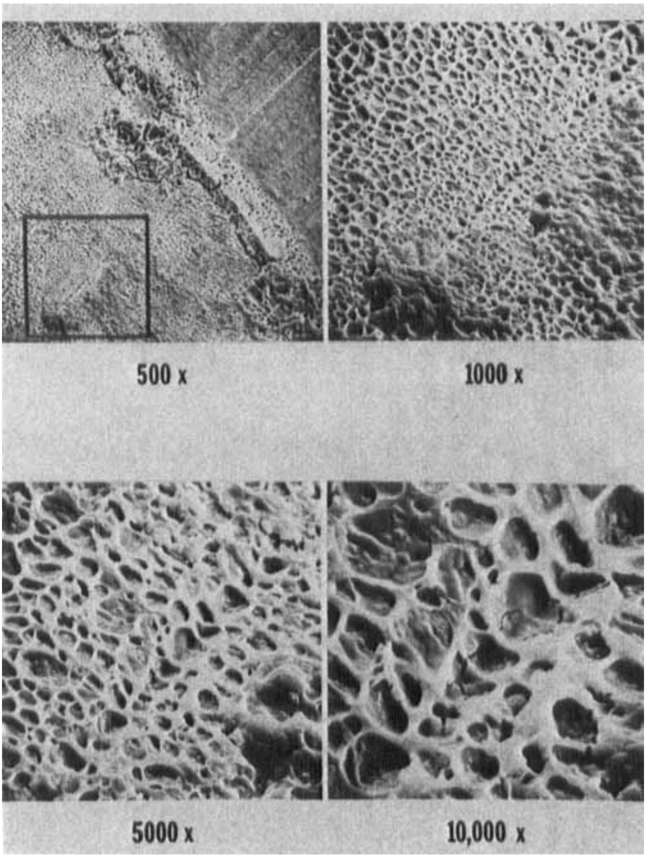

FIGURE 6 Adhesive interface between bovine enamel and cement. Note crack propagating along line of air pockets.

Thus, the topography of the solid substrate affected the manner in which the cement came in contact with the tooth surface and the subsequent microstructure of the hardened cement near the interface. The actual source of the entrapped air may be open to question; however, the inference remains that the grooves in the solid substrate caused the air pockets to concentrate along them.

A concentration of air bubbles may act as weak areas or areas of stress concentration, similar to a sharp edge as previously discussed. In Figure 6, one of the grooves in area 2 is shown at magnifications up to 10,000 ×. At 5000 × and 10,000 × a crack may be observed along the line of bubbles in this groove. The crack down the line of bubbles may have developed during fracture or during drying and metal-coating of the sample. In either case, it is a result of weakness associated with a concentration of air bubbles along the groove. Thus, again the topography of the substrate affected the fracture pattern, even when the cement failed cohesively.

In summary, it has been shown in this investigation that the fracture most likely initiated as an adhesive failure at the interface and that both adhesive and cohesive failure was involved. The topography of the adherend affected the direction and mode of propagation of the fracture, and the topography also affected the wetting process itself by causing entrapment of air at the interface between the cement and tooth structure. In addition, the topography influenced the microstructure of the cement near the interface, since air bubbles in the cement were lined up along grooves in the substrate. Thus, it has been shown that the topography of the adherend does play an important role in the formation of an adhesive bond and in the fracture pattern of an adhesive joint, even when cohesive failure is involved.

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