Hydrolytic Degradation of Dental Composites
and
Effects of Silane-Treatment and Filler Fraction on
Compressive Strength and Thermal Expansion of Composites

From the Department of Dental Technology
Faculty of Odontology
University of Umeå
S-901 87 Umeå, Sweden
Department of Dental Biomaterials
College of Dentistry
University of Florida
Gainesville, Florida 32610, USA
and
Scandinavian Institute of Dental Materials
Forskningsveien 1
Oslo 3, Norway

AKADEMISK AVHANDLING

som med vederbörligt tillstånd av
odontologiska fakulteten vid Umeå universitet
för vinnande av odontologie doktorsexamen
offentligen försvaras i Sal B, 9 tr
Odontologiska kliniken
måndagen den 28 maj 1984 kl. 09.00

av

KARL-JOHN M. SÖDERHOLM
Leg. tandläkare, fil.kand., m. phil.
ABSTRACT


Some researchers have suggested that the weakest link of dental composites is the filler-matrix bond. However, due to incompleteness of information dealing with this bond and its stability in a humid environment, it was considered desirable to investigate the effect of water on this region, as well as the influence of filler bonding and filler fraction on compressive strength and thermal expansion.

Experimental composites containing different filler fractions of either silane-treated or untreated fillers were made. Compressive strength and coefficient of thermal expansion were determined using routine methods, while the hydrolytic degradation was investigated by measuring changes in concentrations of elements in the storage water using atomic absorption spectrophotometry. Scanning electron microscopic investigations were made on fractured samples.

The diffusion coefficient of a representative resin system was determined gravimetrically. Seven commercial composites were investigated regarding hydrolytic degradation. The filler compositions of these composite materials were determined by emission spectroscopy or energy-dispersive x-ray analysis before storage in distilled water. This water was replaced and analyzed monthly using plasma spectrophotometry or atomic absorption spectrophotometry.

After completed water storage the samples were fractured and investigated by use of scanning electron microscopy.

From the results of these studies the following conclusions were drawn:

1. The compressive strength of composites changes linearly with increased filler fraction. Contrary to bonded fillers, composites containing unbonded fillers lost strength with increased filler fraction.
2. Water diffuses through the polymer matrix and attacks the filler particles. This degradation is most pronounced for untreated fillers containing glass modifying elements such as sodium, barium and strontium.
3. The resin, used as a matrix, influences the speed with which the hydrolytic degradation of the filler proceeds.
4. The hydrolytic degradation of the filler seemed to be associated with micro-crack formation occurring in the matrix. Of the investigated composites, the micro-filled resin showed the lowest frequency of such crack formations.
5. The coefficient of thermal expansion decreases linearly with increased filler fraction. Silane treatment did not influence this coefficient.
6. Using a simplified model to predict stresses in a particle filled composite indicates that rather high stress levels are induced in the polymer matrix due to polymerization shrinkage. This shrinkage induces radial compressive and tangential tensile stresses with respect to the filler surface. Increased filler fraction increases the tangential tensile stresses but reduces the compressive radial stresses.

Key words: Internal frictional theory, filler-matrix debonding, stress-corrosion, stress-influenced diffusion, micro-crack formation, crazing, opacity, wear, osmotic pressure, hoop stresses.

K-J. Söderholm, Department of Dental Biomaterials, College of Dentistry, University of Florida, Gainesville, FL 32610, U. S. A.
Some researchers have suggested that the weakest link of dental composites is the filler-matrix bond. However, due to incompleteness of information dealing with this bond and its stability in a humid environment, it was considered desirable to investigate the effect of water on this region, as well as the influence of filler bonding and filler fraction on compressive strength and thermal expansion.

Experimental composites containing different filler fractions of either silane-treated or untreated fillers were made. Compressive strength and coefficient of thermal expansion were determined using routine methods, while the hydrolytic degradation was investigated by measuring changes in concentrations of elements in the storage water using atomic absorption spectrophotometry. Scanning electron microscopic investigations were made on fractured samples.

The diffusion coefficient of a representative resin system was determined gravimetrically. Seven commercial composites were investigated regarding hydrolytic degradation. The filler compositions of these composite materials were determined by emission spectroscopy or energy-dispersive x-ray analysis before storage in distilled water. This water was replaced and analyzed monthly using plasma spectrophotometry or atomic absorption spectrophotometry.

After completed water storage the samples were fractured and investigated by use of scanning electron microscopy.

From the results of these studies the following conclusions were drawn:

1. The compressive strength of composites changes linearly with increased filler fraction. Contrary to bonded fillers, composites containing unbonded fillers lost strength with increased filler fraction.

2. Water diffuses through the polymer matrix and attacks the filler particles. This degradation is most pronounced for untreated fillers containing glass modifying elements such as sodium, barium and strontium.

3. The resin, used as a matrix, influences the speed with which the hydrolytic degradation of the filler proceeds.

4. The hydrolytic degradation of the filler seemed to be associated with micro-crack formation occurring in the matrix. Of the investigated composites, the micro-filled resin showed the lowest frequency of such crack formations.

5. The coefficient of thermal expansion decreases linearly with increased filler fraction. Silane treatment did not influence this coefficient.

6. Using a simplified model to predict stresses in a particle filled composite indicates that rather high stress levels are induced in the polymer matrix due to polymerization shrinkage. This shrinkage induces radial compressive and tangential tensile stresses with respect to the filler surface. Increased filler fraction increases the tangential tensile stresses but reduces the compressive radial stresses.

Key words: Internal frictional theory, filler-matrix debonding, stress-corrosion, stress-influenced diffusion, micro-crack formation, crazing, opacity, wear, osmotic pressure, hoop stresses.
### CONTENTS

1. **PREFACE**  
   
2. **INTRODUCTION**  
   General background  
   The first commercial composites  
   The transition from amalgam to composite resins  
   Development trends  
   Present shortcomings regarding composites  
   Summing-up  

3. **OBJECTIVES**  

4. **EXPERIMENTAL PROCEDURES AND RESULTS**  
   
   I. **RELATIONSHIP BETWEEN COMPRESSIVE YIELD STRENGTH AND FILLER FRACTIONS OF PMMA COMPOSITES**  
      Materials and methods  
      Results  
   
   II. **DEGRADATION OF GLASS FILLER IN EXPERIMENTAL COMPOSITES**  
      Materials and methods  
      Results  
   
   III. **WATER SORPTION IN A BIS-GMA/TEGDMA RESIN**  
      Materials and methods  
      Results  
   
   IV. **LEACHING OF FILLERS IN DENTAL COMPOSITES**  
      Materials and methods  
      Results  
   
   V. **HYDROLYTIC DEGRADATION OF DENTAL COMPOSITES**  
      Materials and methods  
      Results
VI. INFLUENCE OF SILANE-TREATMENT AND FILLER FRACTION ON THERMAL EXPANSION OF COMPOSITE RESINS

Materials and methods

Results

5. DISCUSSION

6. SUMMARY & CONCLUSION

7. ACKNOWLEDGEMENTS

8. REFERENCES
This thesis is based on the following papers, which will be referred to by their Roman numerals:


* Copyright April 10, 1984. Reprinted by permission of John Wiley & Sons, Inc.
INTRODUCTION

General Background

The idea to make a tooth colored restorative material by mixing inorganic filler particles with a cold-curing resin dates back to 1951 (Knock & Glenn, 1951). The justification for adding filler was to reduce polymerization shrinkage, thermal expansion, and water sorption of those resin based tooth colored materials available at that time (Paffenbarger et al., 1953; Rose et al., 1955). However, this precursor to our modern dental composites never became a success. One possible explanation for its poor success might have been that this material was introduced at a time when dentists started to experience some clinical failures with the unfilled resins (Caul & Schoonover, 1953; Kramer, 1954; Hedegård, 1955). Therefore, rather than risk and failures by using the new resin-based, tooth colored restorative material, most dentists returned to the use of silicate cements with which they had at least some previous experience (Paffenbarger, 1972).

Though most dentists returned to the use of silicates, there were some clinicians and researchers who continued to try to find new ways to use the cold-cured resins clinically. A new concept introduced during this period was a method for bonding resins to the enamel by etching the enamel with an acid (Buonocore, 1955). Epoxy resin was proposed at about the same time as an experimental material since it was believed that this type of resin had the potential to bond to tooth structure (Bowen, 1956). An inorganic filler was added to the epoxy resin to reduce shrinkage and to improve bonding along the enamel-resin interface. In 1963, Bowen also introduced the concept of
a coupling agent to achieve a chemical bond between resin and fillers. Although the laboratory results with these experimental materials were very promising, Bowen soon realized that the epoxy resin he was investigating could not be used clinically as it did not cure in a moist environment (Bowen & Molineaux, 1969). To achieve curing intraorally, a new resin was formulated by linking two methyl methacrylate molecules to the two epoxy groups of the epoxy resin molecule. This modification of the epoxy resin was done either by the reaction of bisphenol A and glycidyl methacrylate or by the reaction of the diglycidyl ether of bisphenol A and methacrylic acid. Each of these reactions resulted in the so called BIS-GMA monomer (Bowen 1963, 1965). Through this approach, the epoxy resin was converted to a dimethacrylate which could be polymerized in the same way as the cold-cured methyl methacrylate. Some of the advantages of this monomer compared to previously-used methyl methacrylates include: less polymerization shrinkage, less volatility, and an increased crosslinking potential during polymerization. However, the BIS-GMA monomer proved to be extremely viscous and it was difficult to mix it with fillers without incorporating and retaining a significant concentration of voids. To reduce the viscosity, the BIS-GMA monomer was diluted with other more fluid acrylates such as tetraethylene glycol dimethacrylate before the silane treated fillers were added (Bowen, 1965).

The First Commercial Composites

Although failing to chemically bond to tooth structure, Bowen's resin has served as the matrix for most of the current composite materials
The clinical success of this resin formulation was realized soon after its introduction in 1964 by the 3M Corporation as a commercial product, Addent 35 (Peterson et al., 1966). This success was attributed to the clinical durability of the composites compared to that of the silicates (Bowen et al., 1968; Brauer, 1977). However, the composites exhibited some major clinical shortcomings such as poor color stability, a rough surface which enhanced plaque adhesion, and unsatisfactory wear resistance (Mosteller, 1972; Eriksen, 1974; Phillips et al., 1973). These findings, combined with the previous poor clinical performance of cold-cured methyl methacrylate materials, would have been expected to adversely affect the marketing and development of composite materials. Fortunately, this situation did not occur because of the introduction at this time of the acid etch technique for composite resins (Bjorvatn & Tornes, 1972). The successful combination of the acid etch technique and composite resins made it possible to restore teeth in ways previously considered impossible and helped composites overcome what could have become the first "crisis" (Jordan et al., 1977).

The Transition from Amalgams to Composite Resins

Since the introduction of the acid etch technique, research activity has increased toward the development of improved composites as well as bonding agents (Bowen, 1979; Smith, 1982). This trend is related to the numerous new clinical treatment possibilities that arose from such breakthroughs in dental materials science. Improved wear resistance of composite resins could mean that these products would replace dental amalgam as the most commonly-used restorative material. Since
amalgams have captured approximately 75% of the restorative material market today, the economical aspects of such a transition are obvious. A disadvantage of dental amalgams is that a shortage of metals used in amalgams (tin, silver, mercury and copper) could arise in the near future (Kusy, 1982). In contrast, composites should have a brighter future as the filler constituent used in these materials is available in almost unlimited quantities.

In addition to these important economical aspects, dental composites also possess a color similar to the tooth. As dentistry is continuously concentrating on more-demanding esthetic requirements, we can expect an increased demand from the consumer for these restorations in the future. Another trend in favor of composites is an increased concern from the public regarding mercury toxicity from amalgam restorations (Scholle, 1983). The scientific evidence is inconclusive to justify such a transition to composites at the present time (Dauer & First, 1982). Instead, the extensive clinical experience with amalgam therapy gained during the last century would justify the continued use of amalgams until research has proven that composites are at least as good an alternative as amalgams (Skjørland, 1973; Leinfelder et al., 1983; Stanley et al., 1979).

Development Trends

During the last ten years increased attention has been focused on the development of improved composites. Although research efforts have markedly increased within the past several years, the wear resistance of composites has not improved substantially. These efforts have
resulted in the availability of more products today than ever before, making it quite difficult to select the most suitable material. Several publications have recently summarized information regarding the organic and inorganic components in most commercial composite products (Asmussen, 1975; Ruyter & Sjøvik, 1981; Zinck et al., 1982). These papers show that the most commonly-used resin component is 2,2-bis (p-(2'-hydroxy-3'-methacryloxypropoxy) phenylene) propane, shortened to BIS-GMA, which is diluted with other less viscous monomers such as triethylene glycol dimethacrylate (TEGDMA). To minimize polymerization shrinkage and to insure good color stability of the composite, a minimum diluent content has been recommended (Cowperthwaite et al., 1979; Asmussen, 1981). Against these recommendations are data showing that high BIS-GMA contents result in composite resins with rather low polymerization degree (Ruyter & Svendsen, 1978). There has also been concern for some time among manufacturers about certain problems associated with BIS-GMA. These problems are high water sorption, high viscosity, and low purity (Glenn, 1979). However, during the last ten years, there has also been a trend to replace BIS-GMA with other dimethacrylates. This trend is most pronounced with respect to the production of the so-called microfilled composites in which urethane dimethacrylate resins are commonly used (Ruyter & Sjøvik, 1981; Zinck et al., 1982).

The filler system of most modern composites consists of either quartz, barium and strontium glasses, or pyrogenic silica particles (Zinck et al., 1982). The sizes of these particles range within and between products. Most quartz and glass fillers are 1-10 μm, while the size of the pyrogenic silica, used in the microfilled composites,
are just a few hundred Å in size (Ruyter & Øysaed, 1982; Zinck et al., 1982). A deficiency of microfilled materials is their relatively low filler content, which renders these materials less dimensionally stable in an environment with changes in temperature and humidity. Their low filler content is related to manufacturing problems with incorporating high fractions of microfilled particles into a monomer, since the concentration of microfilled particles dramatically changes the viscosity of the monomer (Jacobsen, 1981). To solve this problem, the manufacturer dilutes the monomer with solvents such as chloroform, adds microfilled particles and evaporates the solvent. By doing so, resins containing a high fraction of microfilled particles can be produced. However, this composite is too viscous to be handled clinically and therefore the manufacturer polymerizes this filled resin and grinds it into organic particles containing the inorganic particles. These composite particles are then mixed as a filler into the monomer and the product is marketed as a microfilled composite, although the organic filler particles could be larger than conventional inorganic filler particles.

In addition to the developments of microfilled composites, manufacturers have recently focused their efforts toward the development of the so-called hybrid or blend composites (Dennison, 1982). These materials are made by admixing micro-fine and more conventionally-sized particles into one resin base, thereby making it possible to increase the filler fraction another 10% by weight compared to the more traditional composites (Dennison, 1982).

Even though the matrix and the filler are the main components of a dental composite, probably the most critical region is the interface
between these two components (Bowen, 1972; Braden, 1978). To achieve a bonding between matrix and filler, the inorganic filler particles are silane treated, in most cases with $\gamma$-methacryloxypropyltrimethoxy silane, in order to form a chemical bond between matrix and fillers (Koelling & Kolb, 1965; Plueddemann, 1970). During the last ten years, attempts have also been made to process fillers with such topography that they would be able to bond mechanically to the resin (Bowen & Reed, 1976a,b; Ehrnfors, 1976).

In addition to these efforts to improve the physical properties of dental composites, attempts to improve the handling properties have also been made. For example, a transition from cold-cured resins toward light-cured resins has occurred during the last several years. During this period, composite resin systems based on a tertiary amine-benzoyl peroxide activator-initiator system were replaced by composites activated by an ultraviolet (UV) light source and initiated by methyl ether of benzoin. Due to concerns about the effect of UV light on oral tissues as well as problems related to the polymerization depth of UV light-cured resin systems, visible light-cured systems were introduced. In these visible light-cured systems, camphoroquinone and N,N-dimethylaminoethyl methacrylate are activated by light with a wavelength of 468 nm (Dart & Nemcek, 1978). Two advantages of this system compared to the UV light system are a lower risk for soft tissue damages and greater polymerization depth, even though the polymerization depth is not completely satisfactory (Swartz et al., 1983). However, risks of ocular damage due to direct and indirect light exposure from the visible light source seem to exist (Antonson & Benedetto, 1984).
Present Shortcomings Regarding Composites

Although composite resins have provided many advantages in restorative treatment through the introduction of the acid etch technique and improved composite systems, composites still are not suitable for posterior restorations except for Class I restorations where esthetics is important (Schrotenboer et al., 1983). The main shortcomings of present composite resin are inadequate wear resistance, discoloration potential, and their possible association with recurrent caries (Leinfelder et al., 1980; Mjør, 1981). Of these drawbacks, the poor wear resistance as well as the possible relationship with recurrent caries have so far restricted the usage of composites to areas subjected to relatively low loads and to locations where it is easy to clean the restoration and its surrounding margins. Regarding recurrent caries, the evidence is not conclusive that the composites available today are inferior to amalgams (Mjør, 1981). In addition to these shortcomings, there are several questions regarding biocompatibility which must be answered before one can state that composites are as safe or safer than dental amalgams (Stanley et al., 1979).

An improvement in wear resistance of composite resins has become the most challenging research problem in the early 1980's. In the dental literature, the wear mechanism of dental composites has been explained as a result of exposure of the inorganic filler by loss of resin matrix. Subsequently, filler particles are debonded and lost, and new resin matrix becomes exposed (Kusy & Leinfelder, 1977). However, this description is too general to explain the basic failure mechanism. The wear process should be analyzed in greater depth to
determine whether there is any specific type of wear mechanism which is dominant. The different types of wear processes are as follows (Burwell, 1957):

1. Abrasive wear
2. Adhesive wear
3. Corrosive or chemical wear
4. Surface fatigue

Abrasive wear can further be divided into either two-body or three-body types. Each of these types can occur in the oral cavity. During sliding of a cusp over and in direct contact with a restoration, a two-body type of wear will occur (Powers et al., 1974). However, if food or any debris is dispersed between the cusp and the restoration, a three-body type of abrasive wear exists (Prasad & Calvert, 1980). Except for abrasive wear, adhesive wear can also occur under high pressure causing local contact points of both occluding cusp and restoration to fuse together followed by a tearing of the surface during dislodging (Craig & Powers, 1976). The third type, called corrosive or chemical wear, might also be a contributing factor, as chemicals could react and weaken matrix, fillers, or filler-coupling agent, thereby facilitating wear of the composite (Bowen, 1972; Söderholm, 1979; Wu & McKinney, 1982). The fourth type of wear, induced by fatigue, is probably also an important process to consider in the breakdown of composites since wear is time-dependent (Draughn, 1979; McCabe & Smith, 1981; McKinney & Wu, 1982).

Regarding these four types of wear, most researchers dealing with the wear of dental composites have focused on abrasive wear (Craig & Powers, 1976). The general findings from these studies have so far
been rather discouraging as the results have not correlated well with results from clinical studies (O'Neal & Eames, 1973; Powers et al., 1974).

To explain these discrepancies between laboratory studies and clinical findings, an increasing number of researchers have suggested that internal stresses as well as fatigue could be the major contributing factors in the wear process (Draughn, 1979; McCabe & Smith, 1981; McKinney & Wu, 1982). Another possibility could also be that chemicals in the oral environment might react with any of the different components of a dental composite (Bowen, 1972; Beech & Brown, 1972; Söderholm & Calvert, 1980; McKinney, 1984). However, no universally-accepted theory has yet been developed to explain the poor wear resistance of dental composites. From available clinical data, it appears that as the most wear-resistant composites are the microfilled materials (Meier & Lutz, 1978; Jørgensen et al., 1979; Christensen & Christensen, 1982; Knudsen & Jørgensen, 1983). In addition to the improved wear resistance of these materials, the microfilled composites can be readily polished with smoother surfaces than any other composite (Dennison et al., 1979).

In addition to the microfilled composites, some strontium glass filler-containing composites have also shown some promising clinical results compared to quartz-containing composites (Moffa & Jenkins, 1978a,b). However, some conflicting data are available regarding the wear resistance of these strontium containing composites (Leinfelder et al., 1982).

Regarding the filler-rich hybrid composites and their wear resistance, too few clinical studies are available to give conclusive
information. However, a recent study indicates that these materials are not superior to other composites (Ameye et al., 1984).

Summing-Up

Although several efforts have been made to improve the wear resistance of dental composites, no substantial breakthrough can be identified since the first commercial composites were introduced. As the coupling agent has remained relatively unchanged, while other resin-filler components have been tried, the weak link could very well be the filler-matrix bond (Bowen, 1972; Braden, 1978). From this viewpoint it is surprising that only a small number of researchers have studied this variable. Fortunately, this interface region has been investigated in aerospace and naval research programs, as fiber-reinforced plastics are very useful materials in these disciplines. From these studies, it has been shown that water can reduce the strength of fiber reinforced resins substantially. Water can also attack glass fibers in a resin matrix, and fiber-matrix debonding as well as crack formation might occur in these materials with time (Erickson & Plueddemann, 1974). Based on this information, it seemed reasonable to investigate the effect of a filler-matrix bonding on compressive strength of dental composites. Since progressive filler-matrix debonding might be induced by either water or thermal fluctuations, these two variables and their influence on the filler-matrix interface were also investigated. A progressive filler-matrix debonding could explain why dental composites fail due to wear after some time in service. Several laboratory studies have shown that composites containing bonded fillers are much more wear
resistant than those with unbonded fillers (Powers et al., 1974, Prasad & Calvert, 1980). In addition to the possible effects of debonding on the wear properties, such a debonding could also influence thermal expansion as a matrix with unbonded filler might expand without restraint in contrast to a matrix with bonded fillers. Debonding would also be able to influence the color of a composite, as stains could be accumulated in filler-matrix gaps. These gaps would in turn influence the opacity of the composite due to a change in refractive index at the filler-matrix interface.
OBJECTIVES

The principal objectives of the present study were:

1. To investigate the influence of filler fraction as well as silane-treatment on the compressive strength of an experimental composite material.

2. To determine the effect of water on the filler-matrix interface to evaluate whether filler-matrix debonding might occur with time in a composite stored in a wet environment.

3. To study the water sorption capacity and diffusion behavior of water in a resin of similar composition as a commercially available dental composite resin.

4. To study effects of water on some commercial products.

5. To determine the filler-leaching behavior of commercial composite resins over a six month period.

6. To investigate the effects of filler fractions and filler treatments on the thermal expansion coefficients of dental composites.
EXPERIMENTAL PROCEDURES AND RESULTS

I. RELATIONSHIP BETWEEN COMPRESSIVE YIELD STRENGTH AND FILLER FRACTIONS OF PMMA COMPOSITES.

The objective of this investigation was to study how volume fraction as well as surface treatment of fillers influence the compressive strength of dental composites.

Materials and Methods

Soda lime glass beads, 4-44 μm in size were used as fillers in these experimental composites. In some composites, these beads were pre-treated with silane. This treatment was done in a 250 ml solution of toluene containing 2 v/o γ-methacryloyloxypropyltrimethoxy silane, in which 50 g filler was stirred for 24 h. The silane-treated filler was then filtered away from the solution and dried at 60°C for another 24 h.

The experimental composite materials were made by adding a predetermined volume fraction filler (10, 20, 30, 40, and 50 v/o) to a 20 ml jar containing some methyl methacrylate monomer. After the total volume of filler had been added, the jar was completely filled with monomer and closed. In order to polymerize the monomer, 1 w/o benzoyl peroxide and 0.3 v/o N,N-dimethyl-p-toluidine were added to the monomer before the filler was incorporated. After the jar had been sealed, the material was mixed in a machine by rotating the jar 5 rpm for about 1 h. Following this procedure, the viscous material was transferred to a syringe and injected into glass rods with an inner
diameter of 4.0 mm. After setting, the materials were heat-treated at 90°C for 12 h, cut and ground to lengths of 8.0 mm, and stored in a desiccator at room temperature. This technique was used to make unfilled PMMA samples.

The 0.2% compressive yield strength was determined on three samples from each group at room temperature using an Instron testing machine and a cross-head speed of 1.27 mm/min. The strength values were analyzed by use of linear regression analysis assuming that a linear relationship between strength and filler fraction existed.

After the compressive strength test, the fracture surfaces were coated with 50 Å of gold and studied in a scanning electron microscope at 10kV. Special attention was paid to investigate the morphology of the filler-matrix interfaces.

Results

A linear relationship was found between compressive strength and volume fraction of filler for $0 < V_f \leq 0.4$, where $V_f$ is the filler fraction for the two composites with different filler treatments ($p<0.01$). The difference between these two kinds of composites was that the compressive yield strength of the composites containing silane-treated filler increased with an increase in volume fraction filler, in contrast to the untreated filler composites. However, when $V_f \approx 0.5$, the compressive strengths of both composites were higher than expected from extrapolating the straight line relationships.
II. DEGRADATION OF GLASS FILLER IN EXPERIMENTAL COMPOSITES.

The purpose of this investigation was to evaluate the effects of water on the stability of the filler-matrix interface in some experimental composites containing soda-lime glass fillers.

Materials and Methods

Four experimental dental composites, all containing about 40 v/o filler, were prepared for study. Two of these materials used cold-cured polymethyl methacrylate (PMMA) as a matrix material while the other two materials used a copolymer of bisphenol A glycidyl methacrylate/triethylene glycol dimethacrylate (BIS-GMA/TEGDMA). The BIS-GMA/TEGDMA composites contained 64 mol% BIS-GMA and 36 mol% TEGDMA and were made to simulate a commercially available composite. This material contained 1 w/o benzoyl peroxide and, in contrast to the PMMA materials, it was heat-cured at 60°C for 1 h, 75°C for 1 h, and 90°C for 4 h, and subsequently it was slowly cooled to room temperature.

Of the two types of composites using the same matrix system, one of the fillers had been silane-treated and the other filler was untreated. The fillers used in all these composites were 4-44 μm soda-lime glass beads. Silane treatment and sample preparation were performed as described in Paper I.

Groups of three samples of each material were stored in 20 ml distilled water in sealed acrylic bottles at 60°C. These samples were fractured by a diametral compressive test after 16, 32, and 180 days in water. After fracture the samples were coated with gold in preparation for scanning electron microscopy.
Another series was designed to determine changes in the pH and the sodium content of the storage water with time. An 80-day storage period was arbitrarily selected and during this time the pH was regularly determined with a pH meter and a glass electrode. The sodium concentration of the storage water was determined at the end of this 80-day period by atomic absorption spectrophotometry, using a hollow cathode lamp, an air-acetylene flame, a 0.7 mm wide slit, and a wavelength of 589.0 nm.

Three dry samples of the BIS-GMA/TEGDMA composite with silane-treated glass beads were cycled in compression with 4400 loads for one hour using a stress level ranging from 0 to 15 N/mm². Three more samples of the same material were cycled for one hour with the same frequency, but with a stress interval of 0-45 N/mm². These specimens, classified as low- and high-stressed samples, respectively, were thereafter immersed in 20 ml distilled water and kept at 60°C for 80 days. The storage water of these samples was also analyzed regarding pH and sodium concentration.

Results
Degradation of the filler, exhibited as a peeling of the filler surface, could be seen on some of the untreated glass beads inside the BIS-GMA/TEGDMA matrix after 16 days in water. This filler degradation was located close to the outer surface of the samples.

After 32 days in water, surface changes of the fillers were seen in all composites with untreated fillers. The defects seen in the BIS-GMA/TEGDMA composites were more pronounced than those in the PMMA composites.
The PMMA composites containing untreated fillers suffered from severe filler-surface degradation after the storage time was extended to 180 days. This degradation reached a depth of about 0.9 μm, and the degraded glass layer had a swollen appearance. In the BIS-GMA/TEGDMA composites containing untreated fillers, the glass surface had a swollen appearance, too.

No direct signs of filler-matrix debonding were seen in composites containing silane-treated fillers. However, less electron dense areas and precipitate-like formations could be detected on some of these beads.

The pH of water in which the different composites had been stored increased with time. This increase was most pronounced for composites using PMMA and untreated fillers, reaching a pH of 9.5 after 80 days in water. It was also demonstrated that the pH increased when the filler had been silane-treated, but to a lesser extent. The increase in pH was remarkably small for the BIS-GMA/TEGDMA composites containing silane-treated filler, but became larger after a series of cyclic stresses.

The sodium ion concentration of the distilled water in which the composites were stored showed an increase from 0.1-0.2 ppm to 5-9.5 ppm after 80 days. No direct relationships could be seen between the silane-treated and untreated filler composites.
III. WATER SORPTION IN A BIS-GMA/TEGDMA RESIN.

The present study was undertaken to determine some water sorption properties of a copolymer used as a matrix in a dental composite. The properties investigated were linear swelling, water sorption capacity, leaching, and diffusion coefficients.

Materials and Methods

A combination of BIS-GMA and TEGDMA resins were mixed and polymerized as described in Paper II. Before polymerization, the monomer was cast into a glass rod approximately 10 cm long and with an inner diameter of 21 mm whereupon the rod was sealed from both ends. After polymerization, five discs, each 0.8 mm thick, were cut and smoothed by polishing the cut surfaces with sandpaper (250, 400, and 600 grit). The samples were weighed and stored in a desiccator until stable weights had been gained. The diameters of the discs were measured with a measuring microscope and the thickness of the discs were measured with a micrometer.

After dehydration the discs were individually stored in Petri dishes containing 10 ml distilled water at either 60°C or 37°C depending on the scheduled treatment. After 15 and 30 min of storage in water, the samples were weighed, whereupon the weight gain was measured every half-hour during the next 1.5 hours, and then every hour during the following 6 hours. Subsequently, the weight gain was recorded every 12th hour until a stable value was reached. From measurements of the diameters of the samples after saturation and cooling to room temperature in water, the linear expansion caused by
water sorption could be determined. The desorption process was studied by storing the water-saturated discs in a desiccator at either 60°C or 37°C, depending upon the designated treatment, and the weight loss was determined according to the same time schedule as used during the sorption studies.

The diffusion coefficients of water into the polymer discs were determined by plotting the $M_t/M_\infty$ ratio as a function of the square root of time where $M_t$ was the weight gain after a time, $t$, and $M_\infty$ was the final weight gain. During desorption, a similar curve was plotted, but in this case $M_t$ was the weight loss after a time, $t$, and $M_\infty$ was the final weight loss after dehydration.

By measuring the changes in weight with time and plotting these results at least for $M_t/M_\infty \leq 0.5$, a straight line could be drawn for the investigated materials. The method of least squares was used to determine the equation for this line. This equation permitted an estimation of the time it took to reach $M_t/M_\infty = 0.5$. Knowing that time, $t_{\frac{1}{2}}$, the diffusion coefficients could be calculated from the relationship,

$$D = 0.049/(t_{\frac{1}{2}}/L^2)$$

where $D = \text{diffusion coefficient (cm}^2\text{s}^{-1})$, and $L = \text{thickness of disc (cm)}$ (Crank, 1957). The diffusion coefficient of the polymer was determined by taking the mean value of the sorption and desorption coefficients as the "true" diffusion coefficient (Crank 1957).
Results

The weight gain occurring during the first sorption at 60°C was 3.39 w/o. The weight gain was 3.68 w/o during the second cycle at the same temperature. This increase in water sorption capacity during the second cycle at 60°C was statistically significant according to the Student's t-test (p < 0.005).

During the first sorption-desorption cycle at 60°C, a 0.31% decrease in weight occurred. During the following sorption-desorption cycle at 37°C, the samples increased in weight 0.07%, which later was lost during the second cycle at 60°C. The linear expansion caused by water sorption was 1.07-1.08% and did not change significantly between the three cycles. During the first cycle at 60°C, the desorption diffusion coefficient was higher than the sorption diffusion coefficient, while the reverse order prevailed during the second sorption-desorption cycle at 60°C (p < 0.05). At 37°C, no statistically significant difference was found (p > 0.05) between the sorption and the desorption diffusion coefficients.

IV. LEACHING OF FILLERS IN DENTAL COMPOSITES

The aim of this study was to investigate the leaching rate of silicon from four commercial dental composites stored in distilled water, to evaluate whether hydrolytic degradation of fillers in commercial products could be detected and related to the leakage of glass-modifying elements such as barium and strontium.
Materials and Methods

Four commercially-available dental composites (Concise®, Profile®, Fotofil®, and Silar®) which contained different filler compositions were selected for study.

The filler fractions of the different composites were determined by weight determination of samples before and after the matrix had been burned away at 575°C (ISO Standard 4049, 1978). The various fillers were analyzed by optical emission spectrography using photographic recording followed by identification of elements based on visual comparison with standards.

X-ray diffraction spectra were taken of one sample of each composite to evaluate whether the filler was crystalline or amorphous.

For the leaching determination six circular discs, 15.0 mm in diameter and 0.85 mm thick, were made of the four composite products. After polymerization, one side of each sample was slightly roughened by sandpaper to assure exposure of filler particles on that side. All six samples of each composite material were placed in a plastic bottle containing 10 ml distilled water and stored in an oven at 60°C. After 30 days, the samples were transferred to another bottle containing 10 ml distilled water whereupon another 30 day period of storage followed.

After the total 60 day period, the water samples for the two 30 day intervals were analyzed by use of plasma spectroscopy to determine the concentrations of Al, B, Ba, Mg, Sb, Sr, Ti, and Si.
Results

Except for the microfilled resin, each composite contained about 0.6 volume fraction filler. The microfilled composite contained only about 0.3 volume fraction filler. The optical emission spectrography analysis showed that Concise® and Silar® mainly contained Si, while Profile® contained Si, Sr and Al. The main constituents of the filler of Fotofil® were Si, Ba and Al.

X-ray diffraction analysis showed that all materials, except Concise®, were amorphous in structure. The crystalline structure of Concise® was identical to β-quartz.

The plasma spectroscopic analysis showed that Profile® released Sr and B, while Fotofil® leaked Ba and B. All materials leaked Si, with the leakage most pronounced for Profile® and Fotofil® during the first 30 days.

Compared to the first 30-day period, the leakage of Sr, B, and Ba decreased during the second 30-day period, as did the leakage of Si. An exception was the microfilled composite, which showed almost twice as high leakage of Si during the second period.

V. HYDROLYTIC DEGRADATION OF DENTAL COMPOSITES

This study was undertaken to evaluate the leaching rate of silicon, strontium and barium from four composite resins during a six month period. Special attention was paid to detect any signs of morphological changes which could indicate ongoing hydrolytic processes at the filler-matrix interfaces.
Materials and Methods

Three composites, P-10®, Profile®, and Den-Mat Class II®, each advertised for use in posterior restorations, and one microfilled resin, Isopast®, were investigated.

Five samples of each material, 15.0 mm long and 4.0 mm in diameter, were individually stored in 7 ml distilled water at 60°C. After thirty days, the samples were transferred to other vials containing 7 ml distilled water while the previously used storage water was kept for future analysis. This process was repeated six times.

Five samples of each composite were ground flat and coated with gold. Analysis of the filler composition was performed using an energy-dispersive x-ray analyzer operated at an accelerating voltage of 15 kV. After identification of the principal elements, the compositions were determined by use of a computer program able to perform a quantitative analysis.

Based on the filler compositions determined by energy-dispersive x-ray analysis, the storage water was analyzed for concentrations of silicon, strontium, and barium. These atomic absorption spectrophotometric analyses were performed by use of hollow cathode lamps and a nitrous oxide-acetylene flame. Silicon, strontium, and barium were analyzed at wavelengths of 251.6 nm, 460.7 nm, and 553.6 nm, respectively, using a slit setting of 0.2 nm. Analysis of variance was performed on the atomic absorption data collected over the six-month period.

Except for the analytical procedures, light microscopy and scanning electron microscopy were used to investigate the morphology of the investigated materials both before and after storage in water.
Results

The energy-dispersive x-ray analysis showed that the filler of P-10® and Isopast® mainly contained Si, while Profile® contained aluminum, silicon, and strontium. The filler composition of Den-Mat Class II® was similar to that of Profile® except for a small barium content and a lower strontium concentration.

The atomic absorption spectrophotometric analysis revealed that all materials were leached of silicon. Except for silicon, Profile® also released strontium while the Den-Mat Class II® composite lost both strontium and barium. A certain proportionality existed between silicon, strontium, and barium. Regarding the leaching pattern of the different materials, an irregular change with time was found except for Isopast®. The greatest and second greatest leaching rate for silicon were demonstrated by Profile® and Isopast®, respectively, while P-10® showed the lowest leaching rate (p<0.05).

Scanning electron microscopy showed that cracks close to or at the surfaces could be seen on P-10®, Profile® and Den-Mat Class II® samples stored in water. Of these three materials, a large number of cracks was observed in Profile® and Den-Mat Class II® specimens but few cracks were found in the P-10® specimens. Isopast® did not show any detectable cracks. The detected cracks were located at the matrix-filler interfacial zone and tended to propagate away from these regions at sharp filler corners to other matrix-filler interfacial areas.
VI. INFLUENCE OF SILANE TREATMENT AND FILLER FRACTION ON THERMAL EXPANSION OF COMPOSITE RESINS.

The objectives of this investigation were to study the effect of filler fraction on the coefficient of thermal expansion and to evaluate the influence of the filler-matrix bond quality on the coefficient of thermal expansion.

Materials and Methods.

Experimental composites, containing 0.2, 0.4 or 0.6 volume fraction of either silane-treated or untreated soda-lime glass beads were prepared for study. The matrix was triethylene glycol dimethacrylate (TEGDMA), to which 0.15 w/o benzoyl peroxide and 0.2 v/o N,N-dimethyl-p-toluidene were added to activate polymerization. In addition to these composites, pure resin samples were also made. These materials were placed into glass tubes 4.0 mm in diameter, cold-cured and cut into 50.8 mm long samples. After curing, the samples were stored at 65°C for 12 h.

The coefficient of thermal expansion of each sample was determined twice in a dilatometer. The temperature range and heating rate for these measurements were 25°C to 90°C and 4°C/min, respectively.

A linear regression analysis was performed on coefficient of thermal expansion versus filler fraction data.

To estimate possible stress levels in a composite at room temperature, a simplified model of a composite containing spherical fillers was introduced. Based on stresses in a thick-walled spherical shell caused by an internal pressure, the highest and lowest stress levels
which might occur in the investigated composite could be estimated with this model. The effect of filler fraction on these stresses could also be visualized from this model by ordinary calculations.

Results

The linear regression analysis showed that the coefficient of thermal expansion of the investigated materials follows a linear relationship with filler fraction ($p < 0.05$). Regarding the different filler treatments, no differences could be detected in thermal expansion for a specific filler fraction. However, thermal cycling seemed to cause a decrease in the coefficient of thermal expansion detected during the second cycle.

Combining the experimental results with the simplified model of a composite presented in this study, it was shown that filler particles are surrounded by hoop stresses induced during polymerization. These stresses are compressive in a radial direction at the filler-matrix interface, while they are in tension in a tangential direction. These stresses decrease with distance from the filler-matrix interfacial zone and become zero in a radial direction at the surface of the proposed composite model. Residual tensile stresses remain in a tangential to the filler surface. The magnitude of these stresses are dependent on filler fraction. Low filler fractions give high compressive stresses and relatively low tangential tensile stresses. Higher filler fractions reduce the compressive radial stresses but increase the tangential tensile stresses.
DISCUSSION

Paper I shows that a good filler-matrix bond is required when a dental composite is made. Lack of such a bond will weaken rather than strengthen a composite material if more filler is added, at least when a spherical filler is used. If the filler is well bonded to the matrix mechanically or chemically, an increase in compressive strength can be expected with an increase in filler fraction (Ishai & Cohen, 1968; Prasad, 1977).

Through the years the general trend has been to use as high a coupled-filler fraction as possible (Dogon et al., 1982). Attempts have also been made to improve the mechanical retention of filler within the matrix (Bowen & Reed, 1976a,b; Ehrnford, 1976, 1981, 1983). The benefits of this increase in both filler fraction and filler bonding have resulted in higher compressive strength and modulus of elasticity, and lower polymerization shrinkage, thermal expansion, and water-sorption/water-swelling of the dental composite (Bowen & Rodríguez, 1962; Bowen, 1964).

Even though larger filler fractions and better filler-matrix bonding improve the properties of composites, it should be noted that the individual composite components retain their original properties (Holliday & Mann, 1966). Accordingly, the inorganic filler does not improve the properties of the resin per se, but merely acts to reduce the undesirable properties of the polymer. Due to great differences in some physical properties of the matrix and the filler, one can suspect that hygrothermal changes as well as polymerization shrinkage could induce relatively large stresses at the filler-matrix interfaces.
(Hahn & Kim, 1978; Harris, 1978). These stresses, as well as chemicals associated with the oral environment, might cause filler debonding from the matrix with time (Söderholm & Calvert, 1980). Thus, the deterioration of the filler-matrix bond with time will determine the long-term properties of a composite restoration. The effect of filler-matrix debonding was also indirectly demonstrated in Paper I. In this study it is shown that the compressive strength of composites containing 0.5 volume fraction of unbonded filler was only one-half the strength of composites with bonded filler. In addition to the significance of good matrix-filler bonding on compressive strength, its effect on the wear properties of composites has also been shown (Powers et al., 1974; Prasad & Calvert, 1980). In one study on wear, it was shown that composites containing unbonded filler wore as fast or faster than the pure matrix material, while composites containing bonded fillers were much more wear-resistant (Prasad, 1977). Accordingly, the poor clinical long-term wear resistance of dental composites could be a result of matrix-filler debonding occurring in the oral cavity with time (Bowen, 1972; Braden, 1978).

To investigate the proposed failure mechanism, several factors such as polymerization shrinkage, hygrothermal incompatibility, and chemical processes must be considered. Before any theory can be proposed regarding such a debonding mechanism, it is important to characterize the filler-matrix interface. The surface between the resin and the filler can be identified as the true filler-matrix interface. However, this surface is difficult to study due to its infinitesimally small volume. As most adhesive bond failures described as interface debonding occur in a region very close to but
not exactly at the true interface, the term filler-matrix interface is in reality synonymous with the interface region. This region includes a thin layer of the filler at the filler surface, the coupling agent, and a thin layer of the matrix at the coupling agent-matrix interface. Each of these components have their own specific physical and chemical properties (Kwei, 1965).

Regarding the silane layer and its ability to bond to the filler surface, most researchers currently agree that its filler bonding ability is either of a covalent or polar nature (Koelling & Kolb, 1965; Plueddemann, 1970). Whether these two types of bonds, especially the hydrogen bond, are stable in an aqueous environment has been an open question for several years in literature dealing with reinforced plastics (Erickson & Plueddemann, 1974). The results presented in Paper II indicate that the silane coupling agent used in this study was stable against water attack over the duration of the study. However, the weak point of the interface region was the surface of the filler particles, which showed signs of hydrolytic degradation, especially when the filler was not silane treated. This degradation is explained by assuming that water reaching the filler-matrix interfaces leach sodium ions from the glass surface (Charles, 1958). As a result of this leaching process, the silica network becomes negatively charged due to loss of positive sodium ions. To compensate for this charge imbalance, hydrogen ions of the water surrounding the glass surface are attracted into the silica network. Through this process, hydroxyl ions of the water accumulate outside the glass surface, thereby increasing the pH in that region. At a certain pH level, these hydroxyl ions attack the siloxane bonds inducing a
hydrolytic degradation of the filler surface. These reactions can be described as follows (Charles, 1958):

\[
\text{-Si-O}^- \text{Na}^+ + \text{H}_2\text{O} \rightarrow \text{-Si-OH} + \text{Na}^+\text{OH}^- \tag{1}
\]

\[
\text{-Si-O-Si-OH} + \text{OH}^- \rightarrow \text{-Si-O}^- + \text{HO-Si-OH} \tag{2}
\]

Thus, the reactions between the hydroxyl ions and the silica network result in a breakdown of the silica structure. As one of these reaction products is \(-\text{Si-O}^-\), water will continue to react with the silica network according to the reaction

\[
\text{-Si-O}^- + \text{H}_2\text{O} \rightarrow \text{-Si-OH} + \text{OH}^- \tag{3}
\]

Due to proton transfer, new hydroxyl ions are formed which continue to react with the silica structure, and hydrolytic degradation thereby becomes autocatalytic (Charles, 1958).

The results presented in Paper II indicate that this type of reaction occurs in all composites studied, as both pH and sodium ion concentration increased in the storage water of all the composites with time.

According to the SEM investigation (II), the untreated fillers in the BIS-GMA/TEGDMA composites showed the first signs of hydrolytic degradation, while the untreated fillers in the PMMA composites showed the most dramatic changes after a six-month exposure to water. This difference might be explained as a result of differences in the diffusion rates of water, sodium, and hydroxyl ions in the two resins.
According to Paper III and a previous investigation by Braden (1964), the exchange rate of water through the PMMA matrix is faster than that through the BIS-GMA/TEGDMA resin. The leaching of sodium from the PMMA composite should then be initiated faster than in the BIS-GMA/TEGDMA composite. Even though the generation of hydroxyl ions as a result of sodium ion-hydrogen ion exchange might be faster in the PMMA matrix, the hydroxyl ions might also diffuse away faster from the filler surface in this material than from corresponding regions of the BIS-GMA/TEGDMA composite. Such a difference in hydroxyl ion diffusion could mean that even though the hydroxyl ion formation inside a BIS-GMA/TEGDMA composite is slower, the critical pH for initiating hydrolytic degradation could be reached sooner inside this composite.

When the critical pH value has been reached inside the PMMA composite, the autocatalytic process and filler degradation could very well proceed more rapidly in the PMMA composite than in the BIS-GMA/TEGDMA composite due to the faster diffusion of water in the PMMA resin. This may be demonstrated through reactions (2) and (3) which show that water is necessary for a regeneration of hydroxyl ions (Charles, 1958). Accordingly, the faster the water molecules reach the filler surface, the faster the autocatalytic process will proceed when it has been initiated.

The results presented in Paper III showed that the diffusion coefficient of water in BIS-GMA/TEGDMA was approximately one-tenth that of PMMA. Regarding the changes in sorption and desorption coefficients between the first and second cycle at 60°C, it has been hypothesized that stresses induced during swelling and dehydration induced surface cracks (Rosen, 1961). However, no attempts were made
to explore this theory through SEM analysis. Further studies of this type should be performed to determine whether or not such crack formation occurs, as such cracks would facilitate wear of the matrix material.

In Paper III, it was further shown that the linear swelling due to water saturation was as high as 1.08%. The swelling process may have either a positive or negative impact on the performance of a composite material (Asmussen & Jørgensen, 1972; Hembree, 1983). Water swelling may compensate for the setting contraction (Asmussen & Jørgensen, 1972). However, excessive swelling could induce stresses at the restoration-enamel interface, contributing to debonding and marginal leakage (Hembree, 1983).

Based on the diffusion coefficients at 37°C and 60°C, and assuming that the Arrhenius relationship is valid in this interval, it is possible to estimate the activation energy for water diffusion in the BIS-GMA/TEGDMA resin. The calculated activation energy value is approximately 10 kcal/mole. This value is almost identical to the vaporization energy of water at these temperatures and may indicate that the energy needed to produce water diffusion through a BIS-GMA/TEGDMA resin is consumed primarily by water vaporization (Moore, 1968). These results imply that the diffusion of water in the investigated BISGMA/TEGDMA resin is a process where water molecules penetrate as water vapor into the network where they are attracted by strong polar groups. When another activated water molecule reaches such a hydrogen-bonded water molecule, it can displace the previously-attached water molecule. In this process, its kinetic energy is lost, and the molecule becomes bonded by the polar group previously occupied
by the displaced molecule. This model indicates that the diffusion of water through this resin could be quite passive regarding chain rotations of the resin (Thomas, 1951).

In Paper IV, the leaching behavior of four commercial composites, Concise®, Profile®, Fotofil®, and Silar®, was investigated. This study was designed to determine whether the hydrolytic degradation, which was reported in Paper II, also resulted with fillers used in commercial products. To be able to test the hypothesis that a glass modifying element such as sodium facilitates the hydrolytic degradation of fillers in composites, two composites containing strontium or barium were selected. These materials, Profile® and Fotofil®, were compared to Concise® and Silar® which contained relatively pure SiO₂ filler. The hypothesis being tested was that Profile® and Fotofil® would exhibit more pronounced leaching than the other two materials. After 30 days in water, the results confirmed the validity of the proposed hypothesis. However, during the second period a decrease in leaching occurred for all materials except for Silar®. The Silar® composites exhibited twice as high a silicon leaching rate during the second period. This finding, combined with the fact that the silicon was leached from the quartz filler in Concise®, created some doubt on whether only one mechanism was responsible for the leaching of glass modifiers and whether breakdown of the silica network was the sole basis for the hydrolytic degradation of fillers in composites (Charles, 1958; Wiederhorn & Bolz, 1970). However, the total filler surface area of the different composites might explain why Silar® released more silicon than any other material. Based on the assumption that Silar® has spherical
fillers 0.04 μm in diameter, while the diameters of the other fillers exceed 1 μm, the amount of leached silicon from the different materials per unit area is smaller for both Concise® and Silar® compared to the other two composites (Zinck et al., 1982). Thus, the hypothesis that leaching of glass modifiers is one of the most important factors in hydrolytic degradation of fillers in dental composites was supported by this study. However, leaching of silicon from fillers in Concise® and Silar® cannot be explained on the basis of this hypothesis, and is instead attributed to water attack of stressed Si-O-Si bonds (Wiederhorn & Bolz, 1970). This type of reaction can be explained by considering the molecular structures of both water and the silica network (Michalske & Freiman, 1982). The water molecule has one electron orbit directed away from the hydrogen atoms. This results in a strongly polar molecule with positive charge centers at the hydrogen ends and a negative charge center at the oxygen atom on the opposite side of the molecule. The polar water molecule can interact with strained Si-O-Si bonds (Michalske & Freiman, 1982; Lawn, 1983). This interaction occurs by the formation of a hydrogen bond between the bridging oxygen of the silica network and a hydrogen atom of the water molecule. After hydrogen bond formation, the negative side of the water molecule interacts with one of the two adjacent silicon atoms. This interaction may involve either van der Waals attraction or some covalent bonding with the positive core of the silicon atom. By proton transfer from the water to the bridging oxygen and a simultaneous electron transfer from the oxygen of the water molecule to the silicon atom, the Si-O-Si bond will fail and two new Si-OH groups will be formed (Michalske & Freiman, 1982, 1983). As
these bonds break, more silicon will be liberated from the silica network (Michalske & Freiman, 1983; Budd, 1961).

Paper IV showed that, except for Silar®, the filler leaching rate was greatest initially and decreased with time. Due to this tendency, the possibility of primary leaching from the ground surfaces could not be excluded, even though this leaching pattern was not exhibited by Silar®. Therefore, Paper V considered the possibility that leaching mainly had occurred from ground surfaces by using samples with much smaller ground to unground surface area ratios than those used in Paper IV. Based on the study in Paper V, it was further decided to treat each sample individually in contrast to those in Paper IV to obtain data which could be analyzed statistically.

In Paper V, P-10®, Profile®, Den-Mat Class II®, and Isopast® resins were investigated regarding leaching of silicon, barium, and strontium. Using the findings from Paper II and Paper IV regarding the effect of glass modifying elements on leaching, and considering the total filler surface per volume unit of the different composites, one would expect that P-10® and Isopast® should show the lowest leaching rate per unit area filler. This assumption was confirmed by the experimental results.

Regarding the changes found in leaching of elements with time, Isopast showed the most regular behavior while the other materials showed a more erratic leaching pattern. These variations were explained as a result of micro-crack formation and propagation to the surfaces of the samples where a sudden release of water occurs. The justification for this explanation was based on microscopic findings, which showed that both Profile® and Den-Mat Class II® specimens had
numerous cracks, while P-10® specimens showed just a few cracks and Isopast® specimens did not show any detectable cracks at all. This explanation suggests that these cracks are caused by a buildup of osmotic pressure at the filler-matrix interfaces (Ashbee & Wyatt, 1969; Ashbee, 1972). This pressure is induced as a result of the hydrolytic degradation of the filler (Ashbee & Wyatt, 1969; Ashbee, 1972). As this pressure increases, it eventually causes filler-matrix debonding and crack growth along filler-matrix interfaces (Ashbee & Wyatt, 1969). Reaching regions with high stress concentrations such as corners of fillers, these cracks would change the propagation direction to satisfy the stress field. Eventually growth would result from that corner through the matrix to another filler-matrix interface. Accordingly, the effect of stress-raising factors such as sharp corners could be an accelerating factor in crack growth in dental composites (Draughn, 1979). Regarding the fact that no cracks are seen in Isopast® specimens does not exclude the possibility that an osmotic pressure was causing a filler-matrix debonding in this material, too. The lack of cracks in this particular material might rather be related to the spherical shape of these filler particles. This geometry may generate a more favorable stress distribution in the surrounding matrix, thereby reducing the risk for crack propagation through the matrix.

Based on these findings, Isopast® and P-10® composite resins may offer some advantages over other composites. These advantages are related to their more inert fillers, which are associated with a slower rate of hydrolytic degradation (Wiederhorn & Bolz, 1970). The spherical fillers of Isopast® resins may be more advantageous compared
to the more irregularly shaped fillers of P-10® resins with higher stress-raising capacity. Another positive feature of the microfilled composite is a structure characterized by microfilled particles surrounded by a prepolymerized matrix. During crack growth inside such an organic filler particle, the crack would sooner or later reach a resin-resin interface and impede further crack growth. Such an interface might be more stable and favorable in a wet environment than the inorganic filler-resin interface. This implies that additional crack growth would not occur as easily as in the other type of composites. Furthermore, as the organic fillers are surrounded by a matrix which shrinks during polymerization, the crack growth inside the prepolymerized filler might be inhibited due to the effect of the hydrostatic pressure induced by the surrounding matrix.

The above results regarding crack growth become quite interesting from a clinical standpoint. Several clinical studies indicate that microfilled composites possess better wear properties than other composites, although the opposite is expected based on laboratory wear studies (Meier & Lutz, 1978; Jørgensen et al., 1979; Christensen & Christensen, 1982). Using a variety of replication techniques and scanning electron microscopy, some clinical studies have further shown that microcracks exist in restorations after some time in service (Kusy & Leinfelder, 1977; O'Brien & Yee, 1980). These cracks have been explained on the basis of a fatigue mechanism, but could very well be an effect of hydrolytic degradation and an increased osmotic pressure. This assumption becomes even more interesting when the clinical wear pattern of Profile® is considered. In a clinical study of this material, it was shown that Profile® exhibited rapid wear on
local areas subjected to high loads, while quartz containing composites showed a more general wear pattern (Leinfelder et al., 1982). The high frequency of microcracks in Profile® could explain its rapid local wear, since the high density of cracks would result in a high probability of crack interactions and failures in small. A composite with fewer cracks, such as P-10®, would experience a lower probability of crack interaction which could result in a slower degradation process, but eventually a larger volume loss of material would occur. This material loss could result in a more general wear pattern (Leinfelder et al., 1982).

Further evidence supporting the proposed theory is contributed by studies in which the opacity of composites has been reported to increase with time (Loeys et al., 1982). This opacity change, which seems to be less pronounced for microfilled composites than for other composites, can also be explained by a debonding and crack formation process (Loeys et al., 1982). Accordingly, when such defects are formed inside a composite, these gaps will possess different refractive indices than adjacent matrix and filler. According to Fresnel's law, crack formation will change the refractive index of the composite making it more opaque (Ringström, 1970). The results presented in Paper V showed that interfacial reactions occurred in all the investigated materials, but that crack growth was most pronounced in Profile® and Den-Mat Class II® specimens, and least pronounced in Isopast® specimens. These differences in crack densities could indicate that the latter material should show the smallest change in opacity with time. This result has been observed clinically (Loeys et al., 1982).
Based on the results in Paper V and previously quoted clinical studies, it seems that microfilled composites in general might possess some advantages regarding their durability in the oral cavity. However, even though these materials may have higher clinical wear resistance, they still might be poor alternatives as posterior restorative materials due to their relatively low inorganic-filler concentrations. The relatively large resin fraction in these materials may result in greater hygrothermal instability which could promote percolation and a higher frequency of recurrent caries (Hembree, 1983).

The effects of silane treatment and filler fraction on thermal expansion were investigated to evaluate how debonding would change the coefficient of thermal expansion of composites containing different filler fractions. The result of this investigation, presented in Paper VI, showed that no significant differences in coefficients of thermal expansion exist between bonded and unbonded filler composites containing a given filler fraction. A reasonable explanation for this seems to be that because the polymerization shrinkage is relatively large, the thermal expansion at 90°C was insufficient to compensate for the initial shrinkage.

Paper VI further showed that a linear relationship between filler fraction and coefficient of thermal expansion exists for the investigated materials. Thus, a composite with low filler fraction is likely to have a substantially higher thermal expansion (Zinck et al., 1982).

Based on a simple model of a composite, where the filler is surrounded by hoop stresses induced by polymerization shrinkage of the
matrix, the stresses existing in the matrix were estimated. From these calculations, it was shown that matrices containing higher filler fractions will have higher tangential tensile stresses at the filler surfaces than composites with lower filler fractions. On the other hand, composites with lower filler content will have higher compressive stresses at that surface. These results become remarkable if the results of Paper V are reconsidered. According to the results in Paper VI, a material with low filler fraction such as Isopast should have lower tangential tensile stresses at the filler surface than the highly loaded P-10, while P-10 and the other two investigated composites should not differ significantly as they contain almost the same filler fractions. Assuming that an osmotic pressure is built up in local regions at the filler interfaces in all composites, and that this process occurs more rapidly in composites containing glass-modifying elements, it may be inferred that tensile stresses which induce radial crack growths and crazing would be developed more rapidly in composites containing a large volume fraction of leachable filler. Accordingly, Profile and Den-Mat Class II should show the first signs of cracking followed by P-10 with its more stable filler. Isopast with a filler similar to that of P-10, would react in a wet environment like P-10, but due to a lower filler fraction and a corresponding lower initial tangential tensile stress, it should take a longer time for Isopast to reach a critical tensile stress level required for initiation of cracks and crazing within the matrix. In addition, the higher compressive stresses normal to the filler surfaces will further counteract the osmotic pressure building up at the filler-matrix interface of the composite with low-filler
content. The higher compressive stress levels and lower tensile stress level of this matrix material will further slow down the diffusion of water through this matrix compared to a resin with lower compressive stress levels but higher tensile stress levels (Crank, 1953). Thus Isopast® should have the lowest frequency of cracks within a certain time interval. This hypothesis was confirmed in Paper V.

Based on the above discussion, it appears that filler composition as well as filler fraction are very important factors to consider in processes leading to hydrolytic degradation of dental composites. The composition of the matrix is also very important, as this composition will influence the basic compressive strength (I), water diffusion rate, degree of water swelling (III), and the thermal expansion (VI) of the composite. As discussed in Papers II and III, diffusion of water and leached elements through the matrix as well as stresses induced due to swelling can also influence the hydrolytic degradation of dental composites. Therefore, it is important to keep in mind that most dental composites use different resin combinations and that these variations should result in different behavior in moist environments. However, as shown in Papers IV and V, filler composition could be equally or even more important, at least with respect to the materials studied. This statement is based on the similarities in leaching behavior between Silar® and Isopast® (IV, V), where Silar® is a BIS-GMA/GMA/TEGDMA based composite, while Isopast® uses a polyurethane matrix. Both composites showed an increase in leakage during the second month contrary to the other materials investigated in Papers IV and V. This finding indicates that filler type and filler pretreatment are probably more important regarding hydrolytic degradation than the variations
in matrix composition of these two composites. However, as the materials identified in Papers IV and V were tested under different conditions, several questions remain to be answered regarding variations in matrix composition and their effect on hydrolytic degradation of dental composites.
SUMMARY & CONCLUSIONS

1. The compressive strength of a dental composite changes linearly with filler fraction, at least up to a certain filler fraction. This linear change might be negative which means that increased filler fraction decreases strength. Such a decrease in strength was found for composites containing unbonded fillers, while silane-treated fillers result in a strength increase with filler fraction. Chemicals able to cause a filler-matrix debonding should then be able to cause marked changes in strength properties of composites.

2. Scanning electron microscopic investigations of fractured composite samples filled with soda-lime glass beads did not show a breakdown of the silane-filler bond after storing the composites at 60°C for six months. However, the composites containing untreated fillers showed signs of progressive filler degradation. This degradation process was explained as a result of a progressive stress corrosion process, resulting in leaching of sodium and a pH buildup. Experiments which were designed to measure changes in both sodium ion concentration and pH support this explanation. These measurements further show that fillers, treated with silane, also react with water although at a slower rate.
3. The type of resin, used as a matrix, influences the speed with which the hydrolytic degradation proceeded. The matrix with the lower diffusion coefficient shows the first microscopic changes on untreated fillers, while the matrix with the higher diffusion coefficient shows a more accelerating filler breakdown after some time. Water sorption/desorption studies of a BIS-GMA/TEGDMA resin further revealed that this resin absorbs more water and swells more than PMMA. Changes in sorption/desorption coefficients after repeated cycles indicate that microcracks might be induced as a result of stresses caused by water gradients inside the matrix.

4. Leaching studies of commercial dental composites support the theory that glass modifying elements accelerate the hydrolytic degradation of fillers in dental composites. However, the hydrolytic degradation occurs also in fillers without glass modifiers, indicating that water can more directly attack the siloxane bonds. The latter reaction is much slower.

Most of the composites being stored in water for half a year show signs of crack initiations and crack growth at filler-matrix interfaces propagating through the matrix. The material showing no cracks was the microfilled resin, while the composites containing barium and strontium glasses showed the highest crack densities. These differences were related to the leaching behaviors of the different fillers, and explained by assuming that osmotic pressures are built up in pockets inside the composites.
5. The coefficient of thermal expansion remains the same independent of the quality of the filler-matrix bond. That finding indicates that the polymerization shrinkage of the matrix is too large to be compensated for by thermal expansion used in this study. A debonding of the filler is therefore unlikely to change the thermal expansion properties of a dental composite and should not contribute to increased percolation. The coefficient of thermal expansion is inversely proportional to the filler fraction of one resin-filler system.

6. Using a simplified model of a particulate-filled composite, it is shown that the stresses induced during polymerization shrinkage can be quite high. Based on this model it can be shown that the matrix of such a material will be in compression in a radial direction and in tension in a tangential direction. Higher filler fractions result in lower compressive stresses but larger tensile stresses. As the tangential tensile stresses will facilitate crazing and crack growth, it seems reasonable to strive toward minimizing these tangential tensile stresses.
ACKNOWLEDGEMENTS

I wish to extend my deepest appreciation and sincere gratitude to:

My supervisor, Professor Maud Bergman, Head of the Department of Dental Technology, University of Umeå, for all support and help given to me during the time I worked at Umeå and until today. Without her help and support this thesis would have been impossible to complete from this side of the Atlantic Ocean.

My chairman, Professor Kenneth Anusavice, Department of Dental Biomaterials, University of Florida for all his support and the time he provided in reviewing the manuscripts. His suggestions were most useful and helped me a lot.

My previous chief, Dr. Ivar Mjör, Director for the Scandinavian Institute of Dental Materials, Oslo, for all his support when I was working at NIOM, but also for all his help and care after I left Oslo.

Ms. Sandy Lloyd, Ms. Margaret Kallevig, Ms. Shirley Burdgess, Ms. Eva Forsgren and Ms. Beatrice Dixon for all the hours they have devoted to the preparation of these manuscripts. Their secretarial support has been excellent, and they truly deserve my greatest appreciation and admiration. Their ability to read cryptic manuscripts is surely remarkable.

All my colleagues and friends at the different institutions where I have worked. They all deserve my sincere gratitude as all of them have in some way contributed to the completion of this work. I would especially like to thank Dr. Paul Calvert, University of Sussex, England, for giving me the basic training in the field of composite
materials; Drs. Arne Hensten-Pettersen, Ingvar Magnusson, Chiayi Shen, Dag Brune and Stig Olsson for fruitful discussions and suggestions; Mrs. Linda Mealiea for some editorial help; Dr. Werner Fischlschweiger and Mr. Sten Stølen for assistance with the scanning electron microscopic investigations; and Dr. Sigurd Melson for his help with some of the chemical analyses.

As representatives for the Faculty of Dentistry, Umeå, Sweden, the College of Dentistry, Gainesville, Florida, and the Scandinavian Institute of Dental Materials, Oslo, Norway, I would like to thank Dean Bo Bergman, Umeå; Dean Donald Legler, Gainesville; and the Board of the Scandinavian Institute of Dental Materials for all support these institutions have provided me with in order to complete this project.

I thank my wife Margareta and my children Maria, Johan, Karl-Gustav and Lina for all their support, encouragements and sacrifices. Without their love and care this work would not have become a reality.

Financial support has been given by a grant from the Swedish Medical Research Council, Grant K77-24R-5085.

Gainesville in April 1984

Karl-Johan Söderholm
REFERENCES


Bjorvatn, K. & Tornes, K. H. Nytt håp for frakturerte fortener; Preparasjonsløs restaurering med "composite materials". Fasett, 1972, 7(No. 4), 5-9.


Jørgensen, K. D., Hørsted, P., Janum, O., Krogh, J. & Schultz, J.  
Abrasion of Class I restorative resins. Scand. J. Dent. Res. 1979, 
87, 140-145.

Knock, F. E. & Glenn, J. F. Dental Material and Method. U.S. Patent 
No. 2558139, 1951.

Knudsen, M. & Jørgensen, K. D. Abrasion of microfill restorative 

Koelling, J. G. & Kolb, K. E. Infrared study of reaction between 
6-7.

Kramer, I. R. H. The relationship between pain and changes in the 
dental pulp following the insertion of fillings. Br. Dent. J. 

Kusy, R. P. & Leinfelder, K. F. Pattern of wear on posterior composite 


Kwei, T. K. Polymer-filler interaction. Thermodynamic calculations and 


