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Properties and Interactions of Oral Structures and Restorative Materials

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Dental and Medical Materials Section
Polymers Division
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National Bureau of Standards
Washington, D. C. 20234

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Annual Report for Period:
July 1, 1974 – June 30, 1975

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Prepared for
National Institute of Dental Research
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U.S. DEPARTMENT OF COMMERCE, Rogers C.B. Morton, Secretary
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Acting Director

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ABSTRACT

A diversity of experimental approaches is being investigated to develop techniques which can be applied in formulation of adhesive restorative and caries-preventive dental materials. A newly developed testing procedure, still in the evaluation stage, has demonstrated expected ranking of adhesive bond strengths within a group of selected coating agents, both coupling and release types. Deterioration on exposure to water of cohesive bond strength in the Bis-GMA matrix has been indicated without concurrent deterioration of the coupling agent. A monomer system with potential as a composite or pit and fissure sealant resin and giving a polymerizable liquid of desired viscosity at room temperature was derived from three low-melting, crystalline isomers of ether-ester linked aromatic dimethacrylates. A series of monomers of varying chemical structure was evaluated for possible application in photopolymerization experiments designed to investigate modification of hard tissue by grafting. Modifications to extend the running time of a dental restorative wear-generating experiment threefold and which allow the computerized recording of ten, instead of two, depth of wear measurements around the circular wear track have significantly reduced the standard error of measurement. Surface coating techniques being developed to strengthen interfacial bonding in dental cements and other dental materials show more promise with titanate than with carbon reinforcing fibers.

SUMMARY

A diversity of experimental approaches has been pursued to develop techniques which can be applied in the formulation of truly adhesive restorative and caries-preventive materials, lack of which remains a major handicap to improved dental health. The approaches include surface characterization, exploration of novel techniques for comparing adhesive strength, synthesis of monomers having selected functional groups, and the modification of tooth and bone surfaces by grafting. Measurements of the wear resistance of restorative materials and dimensional change in tooth specimens as a function of temperature have been made.

Water vapor adsorption data have been determined for a number of dental materials and a procedure developed by which the dry weight of a moisture-adsorbing specimen may be calculated from the data alone. Application of both the Brunauer, Emmett and Teller (BET), as well as the Harkins, Jura (H-J) adsorption equations has been demonstrated. Development of an indirect method of measuring adhesive strength has continued. The method, in which increasing content of variously coated hydroxyapatite filler particles is incorporated into composite test specimens, is being examined for its utility in the comparison of the relative merits of selected candidate coupling agents for use between dental hard tissue and restorative materials. The testing procedure demonstrated aging effects in Bis-GMA, but not in a series of coating agents, on storage in water for one month. With this novel testing procedure, the bond strengths between selected coating agents and synthetic hydroxyapatite were as expected.

In research directed to improving the resin component of today's dental composite restorative system, a monomer system consisting of the three isomeric 2-methacryloxy ethoxybenzoates, each in high purity, has been investigated. From melting point data and certain theoretical relationships, the composition of three binary eutectics was determined preliminary to formation of a ternary eutectic. The system polymerizes to a hard clear resin either with peroxide-amine initiation, or by ultraviolet photo-polymerization. It is a reasonable expectation that resins derived from such ether-ester monomer systems will exhibit enhanced hydrolytic, chemical and UV oxidative stability and will have potential for both restorative and preventive dental application. Using a condensation scheme, several functional monomers (monomers with pendant groups

capable of reaction with dentin or enamel) have been synthesized as crystalline solids. These monomers may have application as adhesive-promoting agents in dental application.

The polyfluoroaromatic methacrylate, 2-methacryloxyethoxypentafluorobenzene, was polymerized by chemical initiator (benzoyl peroxide) and is being investigated for its fluoride-releasing capability by fluoride electrode analysis. This monomer, used as a comonomer with Bis-GMA, may offer potential as a fluoride-releasing pit and fissure sealant system.

A series of monomers of different chemical structure was evaluated for possible application in photo-initiated polymerization experiments designed to investigate modification of hard tissue by grafting. In these experiments, the methyl ether of benzoin was used as the photo initiator. The monoester derivative of 2-hydroxyethyl methacrylate and phthalic acid, as well as a mixture of the monofunctional monomers methacrylic acid and 2-dimethylaminoethyl methacrylate, formed polymer films under UV exposure in 30-40 seconds. A wide range of monofunctional monomers, however, could not be polymerized under these conditions. Methyl methacrylate was copolymerized by photo initiation with several methacrylate monomers having aldehydic pendant groups for increased adhesion to tooth or bone surfaces. The laboratory evaluation of these materials as adhesive-promoting comonomers is in progress.

Coefficient of expansion has been determined on human tooth enamel, dentin and restorative materials. No correlation between direction of the enamel rods and the coefficient of expansion has been observed.

The initial testing of a very limited number of specimens on a wear-simulating apparatus indicated a marked difference between the wear resistance of an amalgam alloy and a composite restorative material analogous to that found by prior clinical service testing. The standard error of the measurement was high and steps have been taken to reduce the variance. By extending the running time of the experiment threefold and allowing for the recording of an increase of fivefold in the number of depth of wear track measurements that could be made around the circular wear track, the scatter of the data has been significantly reduced. Average volume losses per minute per square millimeter of wear couple contact under water at 37°C were 0.23×10^{-3} and 0.13×10^{-3} $mm^3/min(mm^2)$ for composite and amalgam.

To strengthen bonding between the filler particles and the resin matrix of polycarboxylate-type dental cements, several techniques are under evaluation as a means of most efficiently coating both potassium titanate and graphite fibers with a poly(acrylic acid) surface. The techniques involve (1) vapor phase deposition of monomer, and subsequent in situ polymerization, (2) deposition of monomer from a dilute solution of the monomer, followed by in situ polymerization, and (3) deposition of polymer directly from a dilute solution of the polymer. A comparison of the techniques has indicated that the titanate fibers are more susceptible than the graphite to the procedures that have been investigated to date.

INTRODUCTION

The National Bureau of Standards is primarily a measurement organization. Paths from measurement to improved dental service lead from measurement and characterization to development of new techniques for using materials, to laboratory prototypes of improved materials and devices, to clinical evaluation and, finally, commercial production by industry.

The dental research program at NBS is a cooperative effort both in personnel and funding, involving several agencies of government and the American Dental Association. The bulk of other agency support for the total program derives from the National Institute of Dental Research.

The research reported in the following pages is only that portion of the NBS dental program which is supported by interagency agreement.

The objective of the research effort discussed briefly in the following pages is to effect improved dental health through development of new knowledge and better understanding of the mechanical, chemical and physical properties of the components of teeth and bone, as well as materials used or potentially of use in restorative and preventive dental practices.

An outline of the research as approved in the interagency agreement is given below, along with participating personnel.

I. Adhesion of Restorative and Caries-Preventive Materials to Tooth Surfaces
   A. Surface Characterization of Dental Materials by Water Adsorption -- Dr. W. V. Loebenstein
   B. Novel Approach to Development and Assessment of Adhesion in Dental Materials -- Dr. W. V. Loebenstein and Mr. J. W. Kumpula
   C. Synthesis for Improved Adhesion and Stability of Composite Restorative and Sealant Materials -- Dr. J. M. Antonucci
   D. Polymeric Grafting, A Technique for Bonding to Mineralized Collagen Surfaces -- Dr. G. M. Brauer, Dr. J. M. Antonucci, and Mr. D. J. Termini

II. Physical, Mechanical and Physicochemical Properties of Hard and Soft Tissues and of Dental Materials
   A. Dimensional Changes in Tooth Structure -- Mr. G. Dickson and Dr. J. M. Cassel
   B. Wear Resistance of Dental Restorative Materials -- Dr. J. M. Powell and Mr. G. Dickson
   C. High Modulus Reinforcement, Techniques for the Improvement of Dental Cements and Composites -- Dr. J. M. Antonucci, Dr. G. M. Brauer, and Mr. D. J. Termini

I. Adhesion of Restorative and Caries-Preventive Materials to Tooth Surfaces

A. Surface Characterization of Dental Materials by Water Adsorption

There are many facets associated with the characterization of dental materials by the application of adsorption methods. Probably the most widely known characterization is the specific surface of the adsorbent, which is logical since the adsorption process is a surface-related phenomenon. In the case of water vapor adsorption, it is not immediately apparent that the moisture content of an insoluble material (which is certainly a bulk phenomenon) might also be subject to interpretation as a surface property. This is a consequence of the multi-layer aspect of adsorption.

Two well-known adsorption theories, the Brunauer, Emmett and Teller(1) (BET) and the Harkins and Jura(2) (H-J), have been widely used over the past three decades for determination of surface area. The BET equation appears to be somewhat more sensitive, but has the disadvantage of being confined to a relatively small relative pressure (humidity, in the case of water vapor) range; namely, from 0.1 to 0.3. The H-J isotherm equation, while perhaps less sensitive, is applicable over the entire pressure axis. For these reasons, the two theories tend to complement one another. Both isotherm equations have an important property in common. Each is capable of being expressed mathematically as a straight line from which the numerical values of the slope and/or intercept are used to calculate surface area.

Mathematically, two points are required to establish a straight line. Thus, only two adsorption measurements would be needed, providing (a) the experimental points were error-free, and (b) a straight line did, in fact, exist. Since condition (a) is never true, several adsorption points are generally measured. This increases the reliability of the results by affording an estimate of goodness of fit and permitting a least-squares treatment to be made of the data. Since there are now more than sufficient points for the determination of the two required parameters, the data may be called upon to furnish an additional piece of information -

namely, the dry weight of the adsorbent. Since the amount of water adsorbed per g at every humidity point above zero is an implicit function of the dry weight, this latter quantity may be looked upon as an additional unknown constant to be determined simultaneously by an extension of the least squares process. It is significant that no additional experimental measurements are required for this than would normally be obtained in determining only the surface area. It is also significant that the method is capable of predicting the correct dry weight during the desorption (drying) portion of the adsorption-desorption cycle. This is especially significant because an incorrect surface area value would result from desorption data when adsorption-desorption hysteresis was in evidence.

Dental materials, for the most part, were used in collecting the data since their characterization is a primary objective of this work, but the method is perfectly general and not restricted to this specialized field. Apparatus used in collecting data is illustrated in Figure IA-1 and has been discussed in detail in previous reports and in a publication.(3)

It may be seen in some of the results shown here (Table 5) that the dry weight may be calculated by using humidified weights from saturation down to about 50% r.h. This would be especially useful in biological applications where viability of the organism (or tissue) might be destroyed by drying completely.

The amount of water adsorbed per gram at some particular humidity is not an experimental measurement. It is customarily calculated from two measurements: (a) the weight of the sample equilibrated at that humidity, and (b) the weight of the sample equilibrated at zero-humidity - devoid of any adsorbed water - namely, the dry weight. An experimental error in (a) causes an error only in that particular adsorption point. It can frequently be identified and discarded if it departs appreciably from a smooth curve constructed through the remaining points of the isotherm. An experimental error in (b), on the other hand, adversely affects all of the adsorption points and sometimes to such an extent as to make the entire experiment invalid. The present method utilizes all of the (a)-type measurements to calculate the least-square values for (b).

Table 1 lists the surface areas and compares the dry weights calculated by the method of this investigation with experimentally measured values for a number of pulverized dental cements. Also included are the results for barium glass spheres used in the formulation of dental composites. The latter material was measured before and after subjecting the spheres to a 24-hour Soxhlet water extraction. (The resultant increase in surface area

Table 1. ADSORPTION

Low Humidity Range (0.082 → 0.334)

Comparison of BET with H-J for the same data

Expt. #	Material		Surface Area (m^2/g)	Dry Weight g
A444161	Polycarboxylate cement (4 points)			
	Calculated	BET	60.4	1.255
	"	H-J	61.3	1.241
	Experimental	- - - - - - - -		1.249
A444143	Zinc Phosphate Cement (6 points)			
	Calculated	BET	41.8	1.5646
	"	H-J	32.4	1.5703
	Experimental	- - - - - - - -		1.5779
A444164	Zinc Oxide-Eugenol Cement (4 points)			
	Calculated	BET (no convergence)	-	------
	"	H-J	5.2	3.1274
	Experimental	- - - - - - - -		3.1297
A444155	Barium Glass--as received (6 points)			
	Calculated	BET	3.22	1.2886
	"	H-J	3.15	1.2889
	Experimental	- - - - - - - -		1.2895
A444156	Barium Glass--water extracted (4 points)			
	Calculated	BET	8.7	0.9636
	"	H-J	4.6	0.9648
	Experimental	- - - - - - - -		0.9649
A444175	Barium Glass--water extracted (6 points)			
	Calculated	H-J	9.5	0.9646
	Experimental	- - - - - - - -		0.9657

is caused by irregularities in the surface formed by the dissolving of surface ions(4).)

Table 2 illustrates that valid estimates of surface area as well as dry weights are obtainable from desorption (drying) measurements for certain dental materials. This situation arises when the adsorption-desorption hysteresis loop is virtually absent (at least, in the range of humidities within which the experimental measurements are made).

The results of water vapor adsorbed on human dentin are shown in Table 3. Reasonably good agreement in surface area was obtained using both the BET and the H-J isotherm equations. Also, both extremities of the humidity scale were involved in the comparison. The numerical values obtained ranging from 143 to 150 m^2/g are bracketed by values reported in recent publications of 128 m^2/g(5) and 152 m^2/g,(3) respectively.

When the surface area is low, i.e. less than, say, 1 m^2/g, the experimental error associated with the low humidity range becomes relatively high - so high, in fact, that meaningful results may be unattainable. This difficulty can be eliminated in many instances by confining the calculations to the high humidity range. An example of this is illustrated in Table 4 where the material under investigation was a pulverized sample of dental amalgam.

In the final example are included the dry weights predicted, as compared with experimentally measured values for representative dental materials as a result of desorption. Again, the BET equation is not applicable in this range, and the surface areas are shown in parentheses because of the hysteresis effect.

The information contained in the results presented here will be included in a manuscript which has been accepted for publication.(6)

Table 2. ADSORPTION VS. DESORPTION

Expt. #	Material	Surface Area (m^2/g)	Dry Weight (g)
	Poly(methyl methacrylate) (Low humidity range 0.082 ⟶ 0.334)		
A444065	Adsorption (5 points)		
	Calculated:		
	BET	30.4	3.5029
	H-J	24.9	3.4878
A444064	Desorption (6 points)		
	Calculated:		
	BET	(31.6)*	3.5022
	H-J	(29.4)	3.4847
	Experimental		3.5039
	"BIO GEL" (commercial hydroxyapatite)		
A444136	Adsorption (Intermediate humidity** range 0.312 ⟶ 0.804)		
	Calculated (4 points)		
	H-J	43.3	0.3788
A444138	Desorption (High humidity** range 0.926 ⟶ 0.542)		
	Calculated (5 points)		
	H-J	(47.2)	0.3792
	Experimental		0.3802

* Surface area calculations obtained from desorption data are enclosed in parentheses, since they are often not valid.

** These humidities are above the range where BET is valid.

Table 3. ADSORPTION ON DENTIN

Low Humidity vs. High Humidity

Expt. No.		Surface Area (m^2/g)	Dry Weight (g)
A503140	Calculated (6 points 0.082 → 0.334)		
	BET	146	2.0202
	H-J (poor convergence)	---	------
	Experimental		2.0671
A503078	Calculated (5 points 0.082 → 0.312)		
	BET (no convergence)	---	------
	H-J	143	0.2847
A503079	Calculated (4 points 0.334 → 1.000)		
	H-J	150	0.2848
	Experimental		0.2898

Table 4. ADSORPTION - DESORPTION

High humidity range (0.435 - 0.971)

Expt. No.	Material		Surface Area m^2/g	Dry Weight g
	Pulverized Dental Amalgam			
A444124	Adsorption (7 points)			
	Calculated	H-J - - - - -	0.44	5.6135
A444126	Desorption (4 points)			
	Calculated	H-J - - - - -	(0.74)	5.6132
	Experimental	- - - - - - - -		5.6145

Table 5. HIGH HUMIDITY DRYING (DESORPTION) CURVES FOR PREDICTING WATER CONTENT

Expt. #	Material	Surface Area (m^2/g)	Dry Weight (g)
A444153	Barium Glass - as received (Humidity range 0.926 → 0.435)		
	Calculated (6 points) H-J	(2.5)	1.28897
	Experimental		1.28947
A444158	Barium Glass - water extracted (Humidity range 0.971 → 0.435)		
	Calculated (7 points) H-J	(3.4)	0.9663
	Experimental		0.9657
A503091	Commercial Synthetic Hydroxyapatite (Humidity range 1.000 → 0.757)		
	Calculated (5 points) H-J	(117)	0.2612
	Experimental		0.2733
A503136	NPG-GMA Coated Hydroxyapatite (Humidity range 1.000 → 0.542)		
	Calculated (7 points) H-J	(25)	0.4788
	Experimental		0.4805

B. Novel Approach to Development and Assessment of Adhesion in Dental Materials

An indirect tensile strength testing procedure is under development for assessing and comparing the relative merits of candidate coupling agents for use between dental hard tissue and either resin or resin-containing composite restorations. A detailed description of the testing method was given in the Annual Report for July 1, 1973 - June 30, 1974. Briefly, the indirect method consists of dispersing measured amounts of a finely divided synthetic commercial hydroxyapatite (HA) uniformly throughout the monomer prior to polymerization. Before this is done, however, the HA powder is precoated with the candidate adhesive agent to be tested. Tensile strength measurements are then performed on the polymerized specimens. The advantages of this indirect method may be: (1) better interface reproducibility, (2) ability to make replicates, (3) randomization of forces, (4) speed of specimen preparation, and (5) reproducible application of bonding agent. Perhaps its most important advantage is the introduction of an additional dimension (or degree of freedom). This is manifested by a two-dimensional plot of specimen tensile strength as a function of weight fraction of the particulate phase for each series of tests using the same coupling agent.

Each series would always include some specimens containing resin, only, i.e. zero weight fraction of particulate. The choice of amorphous HA (as opposed to a fibrous state) minimized any geometric enhancement which might have masked the interpretation of the effect of the coupling agent being tested.

Replicate specimen preparation provided a mechanism for estimating experimental error under various conditions. This could be used to assess by standard statistical methods, conditions under which polymerization was initiated, tensile testing techniques employed, etc., in order to obtain the best reproducibility possible.

One of the results obtained was the effect of shelf life of monomer formulations on the tensile strength of the polymerized Bis-GMA specimens. The monomer formulations were prepared to contain either aromatic amine accelerator or benzoyl peroxide initiator, and polymerization resulted on mixing equal amounts of the two formulations. The tensile strength of the polymer specimens was observed to increase slightly up to about 7 months of monomer formulation shelf time and decreased thereafter to approximately one-half that attained with non-aged formulations. This is portrayed in Figure IB-1. The explanation for these formulation aging effects has not been determined. The effects observed may possibly relate to an optimum in the ratio of amine to peroxide, this ratio for undetermined reasons changing as a function of the age of the monomer formulations employed. Studies(7) have shown that the speed of polymerization of this monomer system may be optimized by control of the amine/peroxide ratio.

It has been pointed out in the preceding annual report why the weight fraction of particulate raised to the 2/3 power should result in a more linear plot of tensile strength than the weight fraction itself. This has been confirmed time and again by experiments, although in some extreme instances (when the so-called coating agent was, in fact, a "release agent") some curvature still remained. The reasonableness of the 2/3 power relationship can be demonstrated by superimposing on the zero-weight fraction values of Figure IB-1 the corresponding least-square intercepts (shown in (+) signs) in Figure IB-2. Where only a single point appears in the printout, the dual points are in virtual coincidence.

Determination of the effect of aging specimens in an aqueous environment is not influenced by the aforementioned monomer aging. This is because the pair of polymerized specimens to be compared were prepared at the same point in time. In every series tested, the result of a one-month soaking in distilled water at room temperature reduced the cohesive bond strength of the Bis-GMA polymer, while having virtually no effect upon the coating agent. This is discernible from Figure IB-3 corresponding to average tensile strength values for specimens containing a Silane coating agent (SI-1) described by its manufacturer as "polymeric silicone fluid containing some unhydrolyzed chlorine silicon bonds." The asterisks in Figure IB-3 correspond to tensile strength of the originally polymerized composites, while the dots represent the strength of samples after exposure to water for a month. Note that the lower points do not fall off more rapidly (than the upper group) with increasing particulate composition as they would if the coating agent had been weakened.

It cannot be assumed that the weakening of the cohesive bonds of the polymer from a one-month's water immersion was virtually complete within that period of time. In some of the later series, a sufficient number of one-month sample test specimens were water-soaked for an additional month. Figure IB-4 shows that the specimen tensile strength for composites containing HA with an aliphatic acid coating agent (AF-1), after soaking for two months (asterisks) was consistently weaker than for those which had been water-soaked for only one month. The relative positioning of the points in an almost parallel manner again confirms that these results are a consequence of the weakening of the cohesive polymer bonds and not of the interfacial bonding involving the coating agent. Improved polymer casting experience has enabled a sufficient number of specimens to be prepared for comprehensive comparisons to be made between the centrifugal tensile strength apparatus developed in this laboratory and the conventional INSTRON testing machine. Both type test specimens were polymerized at the same time from each mix and samples were prepared in duplicates for different composite compositions of sample AF-1 and all samples tested after one-month exposure to distilled water. The results plotted in Figure IB-5 disclose a one-to-one correspondence between the two tensile test methods.

It is clear that the rate of decrease in tensile strength, when expressed as a function of the surface concentration of particulate phase (i.e. $f^{2/3}$), is a measure of the weakness of the adhesive bonds of the coating agent: the steeper the slope, the poorer the adhesive. Of the various coatings selected, two were chosen with the expectation of performing well. They were NPG-GMA, the addition reaction product of N-phenyl glycine and glycidyl methacrylate developed by R. L. Bowen(8), and TI-1, a new commercial coupling agent consisting of isopropyl-triisostearic titanate.

In addition, three coating agents were chosen to be representative of poor or mediocre adhesive properties. They were AF-1, an aliphatic fatty acid (oleic) characterized by a long straight chain with a weak link (double bond) and a single carboxylic acid group on the end, and two commercial preparations designated by their manufacturers to be non-adhesive; FL-1, a straight-chain highly fluorinated primary alcohol, dihydro per fluor octanol; and SI-1, a commercial silane-containing mold-release agent, described earlier. In addition to these five coating agents, one series of experiments was run with no agent whatsoever.

From a comparison of the steepness at which the tensile strength fell off as a function of weight fraction of particulate, the order of adhesive bond strengths would be:

(NPG-GMA) > (TI-1) > (uncoated) > (AF-1) > (FL-1) > (SI-1)

which is entirely consistent with the expected performance. Only minor changes in the order of decreasing adhesion are found for the series after one-month soaking in water.

It should be pointed out that additional work will be necessary in order to increase the reliance on this method before it can be adopted as a standard procedure. The scatter of the points, in particular, must be diminished appreciably. This problem seems to hinge on the polymerization process, probably to a greater extent than on other factors. A different method of initiating polymerization is being evaluated at the present time.

Some of the conclusions arrived at by interpretation of the tensile strength dependence on particulate weight fraction are subject to confirmation by independent methods. Wherever possible, this will be done.

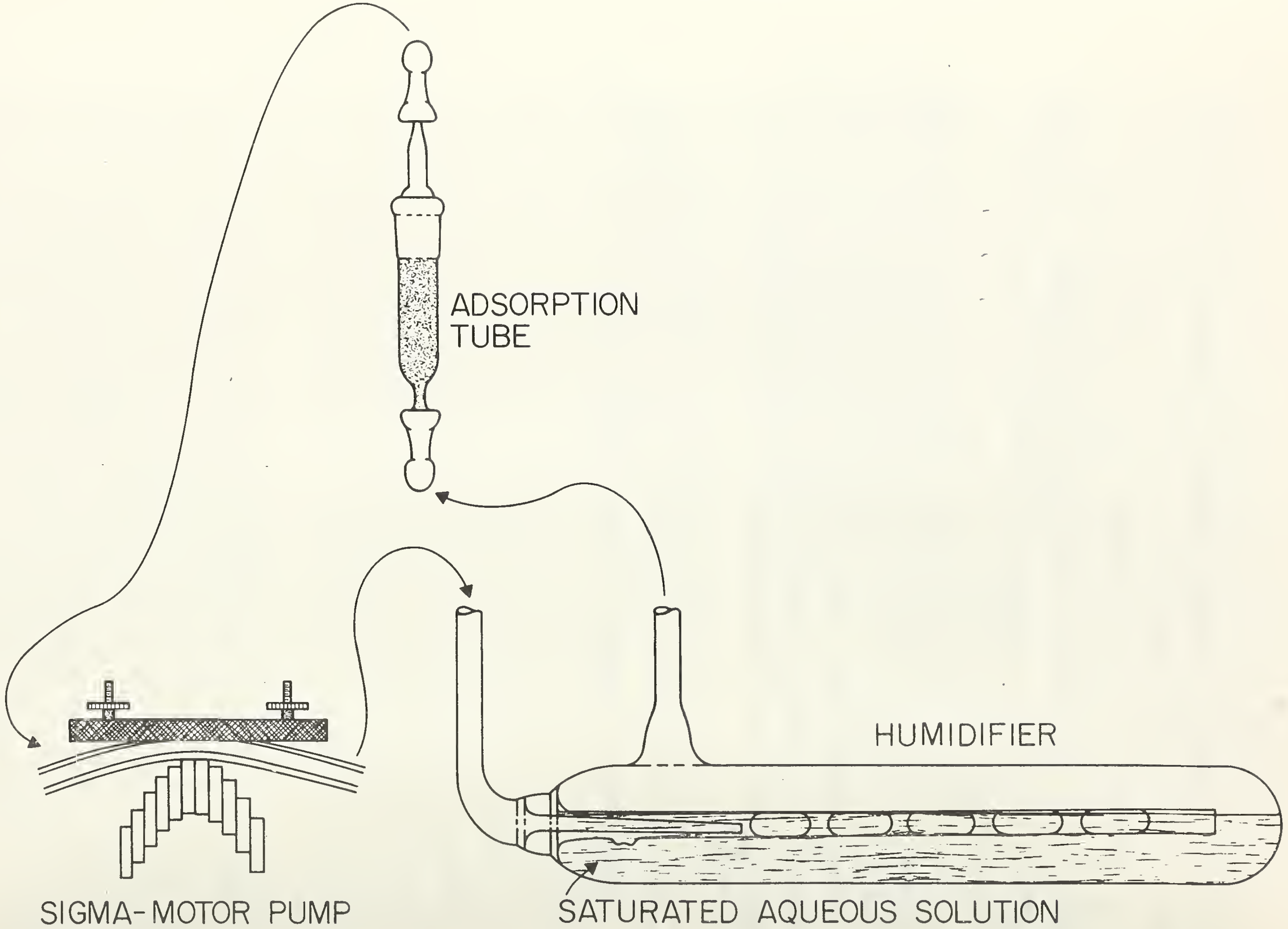


Figure IA-1. Apparatus for gravimetric measurement of water adsorption.

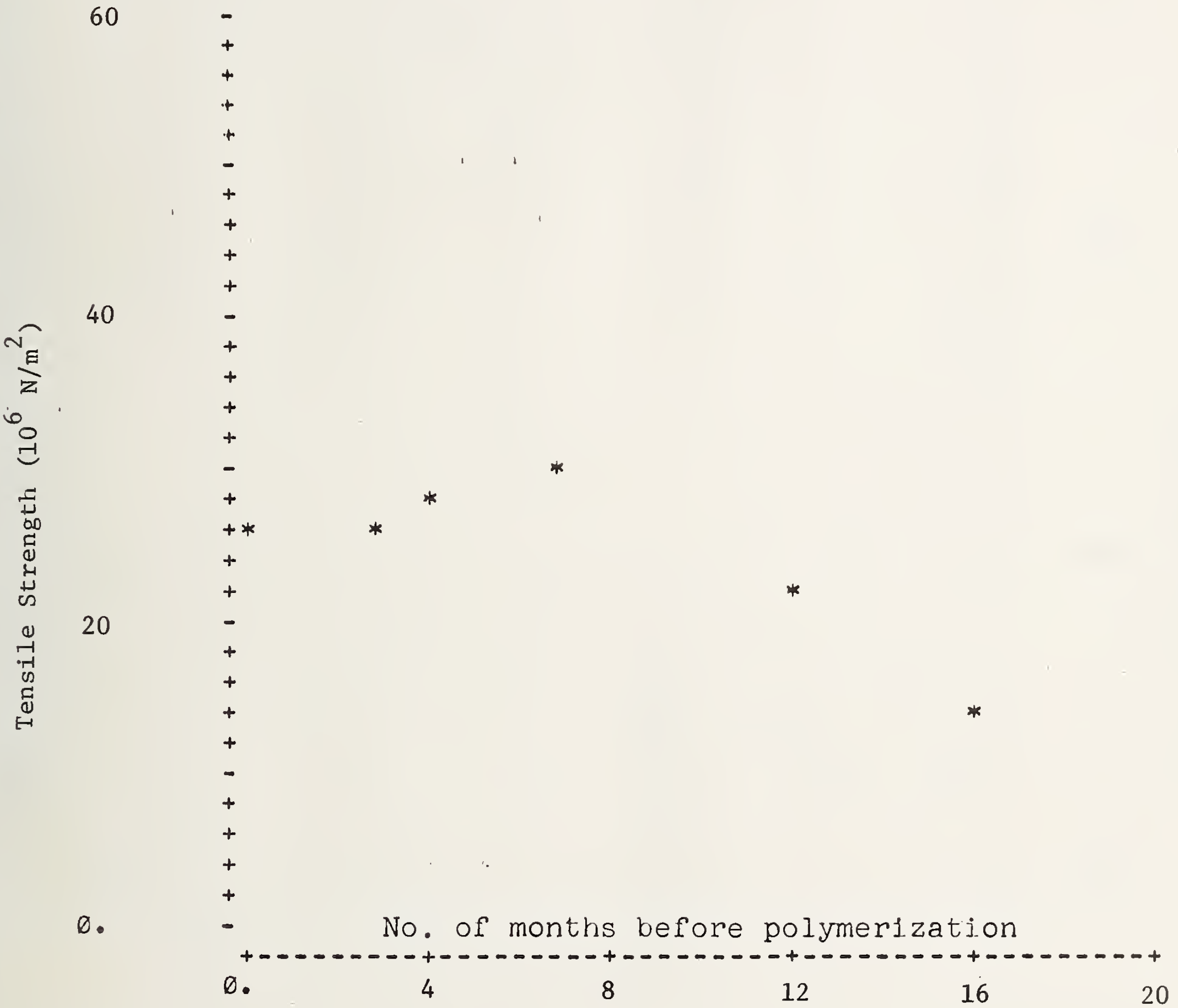


Figure IB-1

The influence of storage time of peroxide-containing and amine-containing monomer preparations on the tensile strengths of freshly polymerized Bis-GMA. (The comparison covers a total span of sixteen months.)

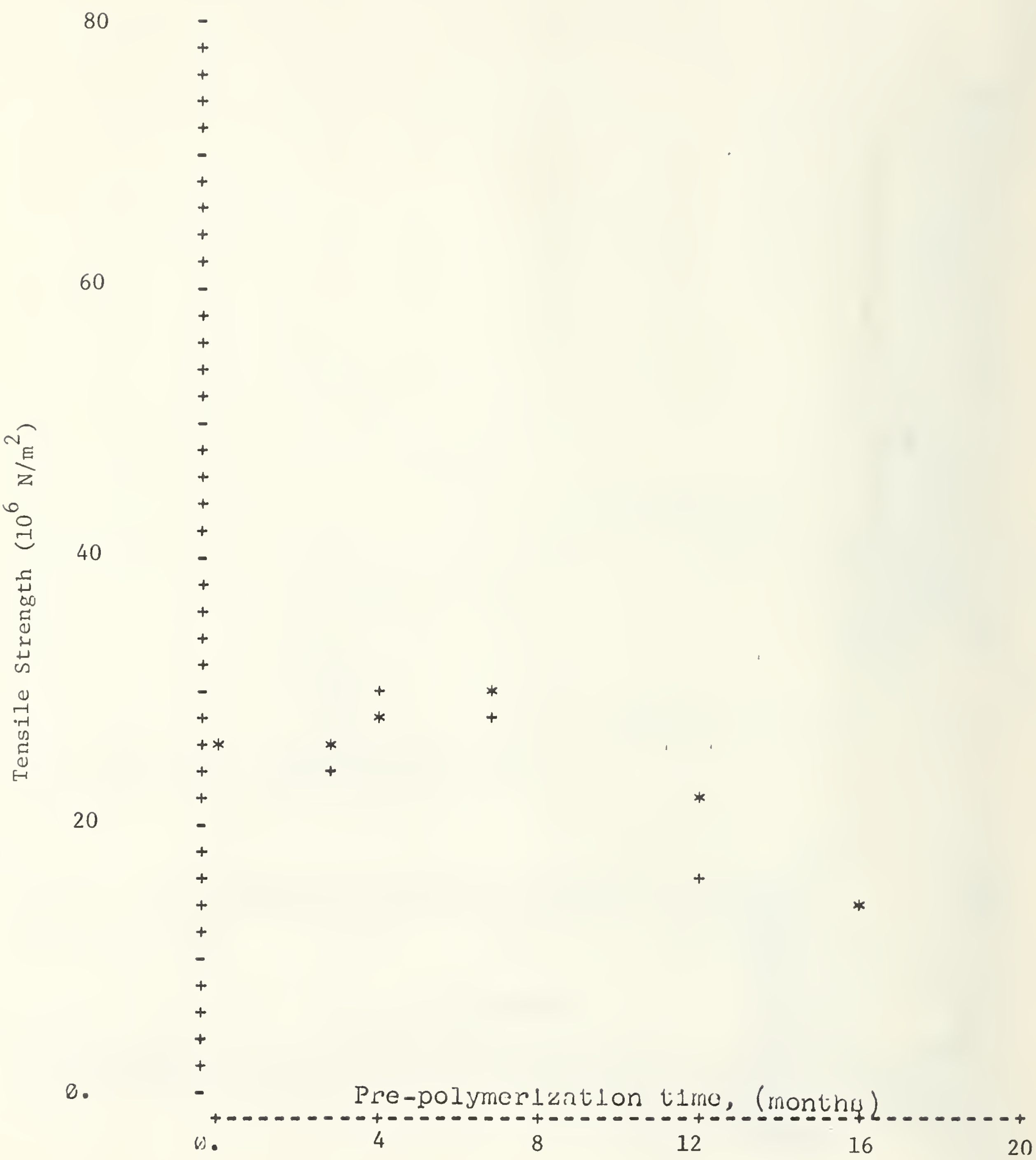


Figure IB-2

Similar to Figure IB-1, but showing the comparison between experimental polymer-only points (Asterisks) and values extrapolated from least-square fitted coated-hydroxyapatite composites (Plus Signs). Each extrapolated point was obtained from a different coating agent series. (Where asterisk-only appears, the two values are in virtual coincidence.)

Figure IB-3.
Effect on tensile strength of a one-month exposure to an aqueous environment at 23°C for composites containing different surface concentrations of a silane-coated hydroxyapatite (SI-1). (Dots correspond to the water-exposed specimens)

*Surface concentration is defined here as the weight fraction (a dimensionless quantity) of the particulate phase raised to the two-thirds power.

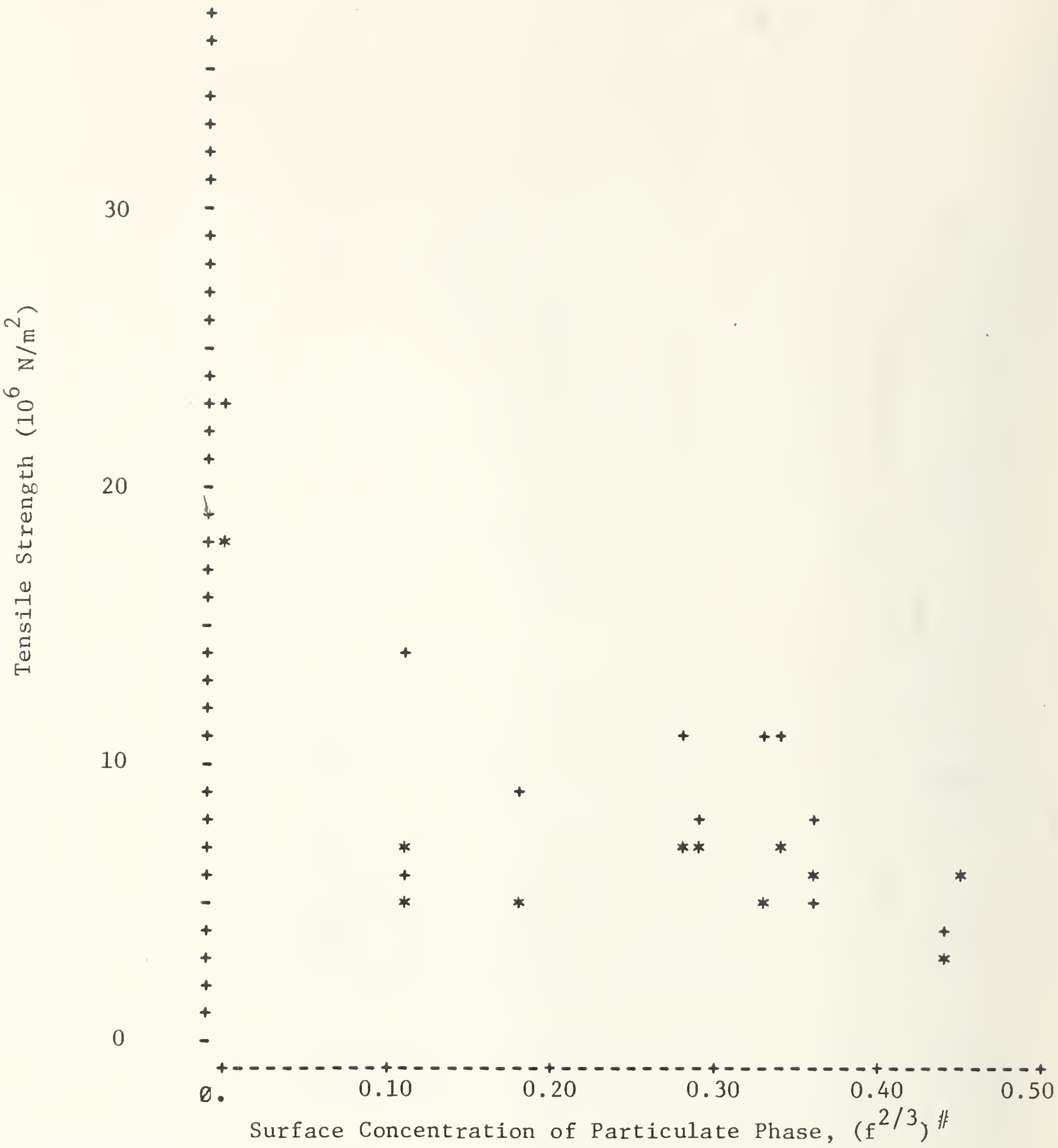


Figure IB-4.
Comparison similar to Figure IB-3, but made between a one-month water exposed (Plus Signs) and a two-month water exposed composite series containing different surface concentrations of an oleic acid-coated hydroxyapatite (AF-1). Except for the zero concentration, all two-month water exposed data (*) represent single values. One-month water exposed data (+) represent averages of two or more specimens.

Surface concentration is defined here as the weight fraction (a dimensionless quantity) of the particulate phase raised to the two-thirds power.

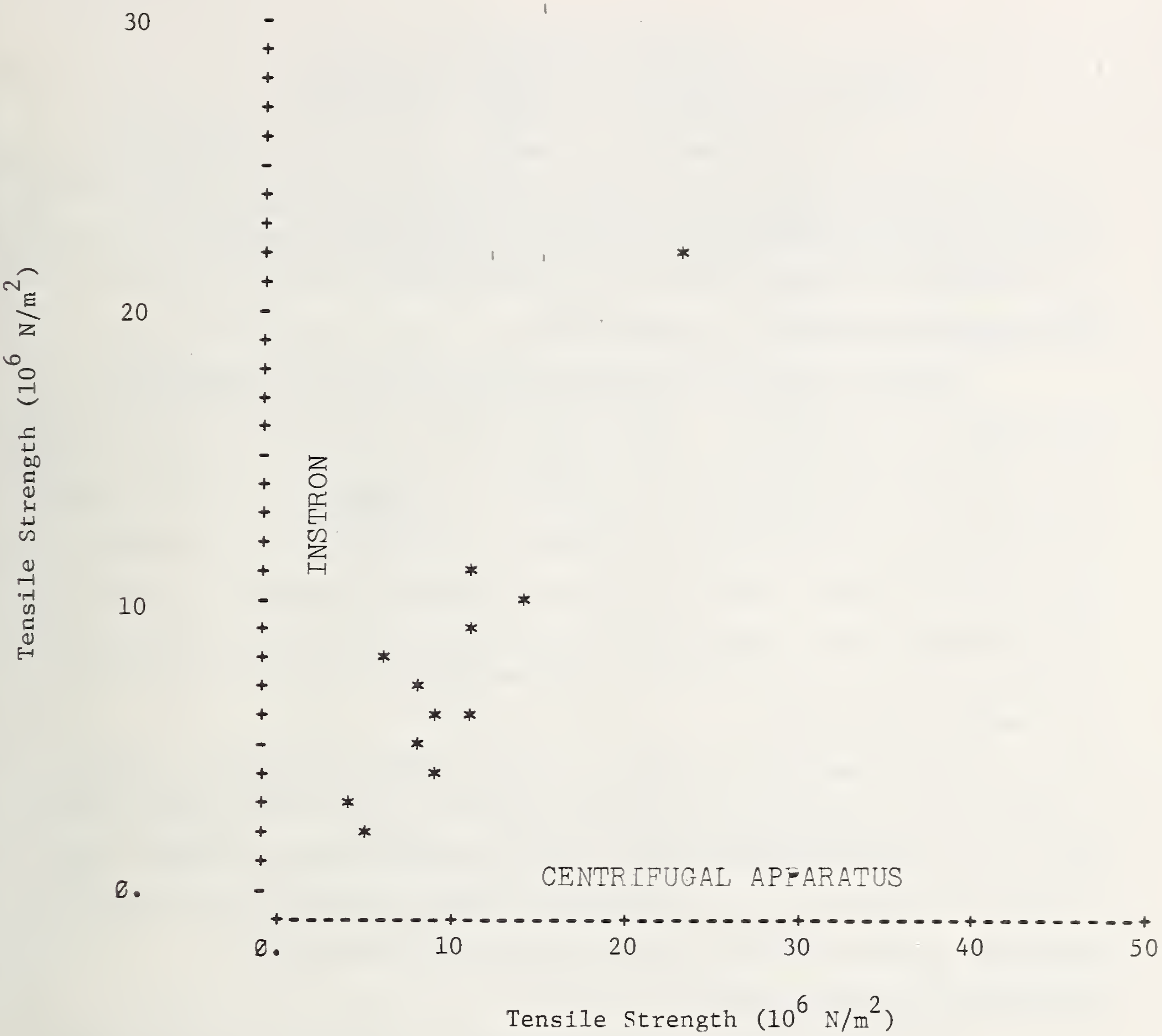


Figure IB-5.
A one-to-one correspondence is found between the commercial Instron tensile strength apparatus and the experimental Centrifugal Instrument for specimen samples polymerized from the same mixes.

C. Synthesis for Improved Adhesion and Stability of Composite Restorative and Sealant Materials

The resin, Bis-GMA, the polymeric basis of all commercially produced dental composite restorative materials, has certain deficiencies, the most important being its excessive viscosity, which requires addition of a dilutent for application in the dental office, and its inability to be produced commercially in pure form.

Previous research by Bowen of this laboratory(9) resulted in development of methods for synthesizing three crystalline and highly purified dimethacrylate esters of the isomeric phthalic acids. Mixed in proper proportion, a ternary eutectic liquid at room temperature, was obtained. High purity and an acceptable viscosity were factors which encouraged the use of this system. However, a color instability, traceable to formation of a charge transfer complex with the tertiary aromatic amine employed as an accelerator in the polymerizing system made the system unacceptable for dental application.

To circumvent the charge transfer complex formation, a system consisting of bis(2-methacryloxyethyl) ethers of the three isomeric aromatic diols (hydroquinone, resorcinol and catechol) was developed. The system has promise and it is currently being investigated for its potential as a field composite system for the Army Dental Corps.

Ether-Ester Dimethacrylate

In the past year, efforts have been concentrated on the aromatic ether-ester dimethacrylate system. The three crystalline monomers are conveniently synthesized by the facile condensation reactions involving hydroxybenzoic acids and 2-bromoethyl methacrylate. As predicted, the isomeric monomers have relatively low melting points and may be highly purified by recrystallization techniques.

Highly purified samples of the three isomeric 2-methacryloxyethyl 2-methacryloxyethoxybenzoates were characterized by NMR and IR analyses. Both analyses support the proposed structures. A carbon-hydrogen analysis was in agreement with the stoichiometric formulae. Melting points of the individual monomers are listed below:

Monomer	M.P.(C)
MoM	34-35
MmM	49.5-51
MpM	50-51.5

MoM = 2-Methacryloxyethyl-o-(2-methacryloxyethoxy)benzoate
MmM = 2-Methacryloxyethyl-m-(2-methacryloxyethoxy)benzoate
MpM = 2-Methacryloxyethyl-p-(2-methacryloxyethoxy)benzoate

From these melting points and the theoretical relationship shown below, the composition of the three binary eutectics was estimated:

Binary	Proportions*	T_e (C)
MoM/MmM	76/24	27
MoM/MpM	77/23	27
MmM/MpM	49/51	33

* Theoretical proportions

$$X_1 = \frac{100\ (T_2 - T_e)}{T_1 + T_2 - 2T_e}$$

where X_1 is the predicted mole % of the lower melting component in the eutectic, T is the m.p. of the lower melting component, T_2 is the m.p. of the higher melting component, and T_e is the eutectic temperature (first sign of melting of the binary mixture).

The three binary diagrams were incorporated into a triangular ternary diagram to arrive at the ternary eutectic. The following three ternary mixtures gave liquids of moderate viscosity at 25°C.

1. 50% MoM, 25% MmM, 25% MpM - solidified at 5°C.
2. 60% MoM, 20% MmM, 20% MpM - liquified at 5° after several months.
3. 68% MoM, 16% MmM, 16% MpM - solidified at -15°C, to be tested at 5°C.

It is interesting that this monomer system may exist in the liquid state at room temperature for a range of compositions. This property may make it possible to obtain improved storage stability of this monomer system by proper choice of composition. For example, a mixture that is liquid near room temperature, but frozen solid when refrigerated, probably would have less tendency toward inadvertent polymerization or oxidation on prolonged storage than a similar mixture that exists as a liquid at the storage temperature as well as at room temperature.

Ternary Mixtures with Amine Accelerators

In contrast to the aromatic diester dimethacrylates (phthalate monomer system) which form yellow charge-transfer complexes with the usual tertiary aromatic amines commonly employed as polymerization accelerators, the aromatic ether-ester dimethacrylates do not discolor on exposure to such amines.

Polymerization

These liquid monomeric mixtures undergo facile polymerization to hard, clear, glossy resins in less than five minutes when initiated with benzoyl peroxide plus N,N-dimethyl-p-toluidine. The same monomer mixtures, when activated by the methyl ether of benzoin, undergo ultraviolet photopolymerization in about 30 seconds to yield a clear, tough sealant film. This monomer system, with its already workable viscosity, may have advantages over the widely used sealant system of Bis-GMA thinned with methyl methacrylate (MMA). No increase in viscosity should occur using the ether-ester system since it is non-volatile. The Bis-GMA system can change in viscosity if care is not taken to guard against volatilization of MMA.

It is encouraging to note that poly(ethyleneoxybenzoate), a linear ether-ester polymer derived from p-hydroxybenzoic acid and ethylene oxide, is reported to have excellent resistance to sunlight, weather and chemicals - comparable with, and possibly better than, that of polyethylene terephthalate, the analogous ester-ester linear polymer.

It is a reasonable expectation that resins derived from the ether-ester monomer system will exhibit enhanced hydrolytic, chemical and UV oxidative stability. To understand what effect, if any, electron donating and electron withdrawing ring substituents have on such polymeric properties as hydroxylitic, oxidative and color stability, a comparative study of the resins derived from the aromatic diester, diether and ether-esters dimethacrylates should be made.

Functional Monomers

Monomers having pendant functional groups capable of reacting or interacting with enamel and/or dentin are classified as functional monomers and may serve as adhesion-promoting agents in dental applications. For example, a monomer or polymer carrying the hydrophilic carboxylate group is functionally capable of reacting with enamel (e.g. polycarboxylate cements).

Unlike the polycarboxylate cement, the functional monomer also would react with the resin monomer system to give polymers that are not water soluble or swellable to any great extent. Consequently, such monomers should lead to more hydrolytically resistant bonding between resin and enamel.

It has been previously shown in this laboratory that the methacryloxyethyl ester of p-hydroxybenzoic acid significantly improved the adhesion between a restorative resin and dentin.(10) Originally, this ester methacrylate was synthesized by the acid catalyzed condensation of hydroxyethyl methacrylate with p-hydroxybenzoic acid. The monomer obtained by this route, however, has proved difficult to purify by recrystallization.

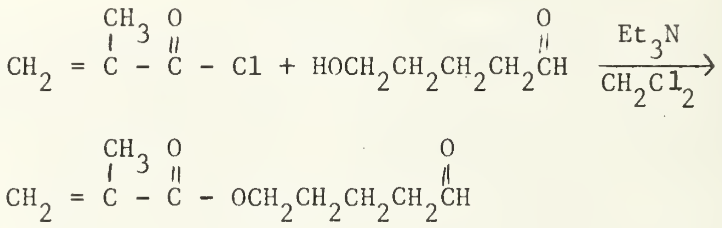
An alternate synthesis of this functional monomer by the condensation of the potassium salt of p-hydroxybenzoic acid and 2-bromoethyl methacrylate has yielded a crystalline solid, m.p. 82-84°C. The monomer has been characterized by NMR and IR analysis.

By a similar condensation scheme, but employing a double salt of p-hydroxybenzoic acid with 2-bromoethyl methacrylate and using mild reaction conditions, p-methacryloxyethoxybenzoic acid, m.p. 141-142°, was formed. The IR spectrum was consistent with the proposed structure.

An interesting functional monomer having a pendant carbonyl $(C\overset{O}{/\!/}H)$ group was synthesized also by the condensation of 2-bromoethyl methacrylate and p-hydroxybenzoyldehyde in the presence of potassium carbonate in an aprotic solvent. The solid monomer, m.p. 47-48°, has been characterized by IR and NMR. It undergoes polymerization on heating somewhat above its m.p. to give a hard, glassy polymer. Some of the polymer appears to be crosslinked, as most of it fails to dissolve in the common organic solvents (e.g. acetone, methylene chloride, tetrahydrofuran). Apparently, the carbonyl group participates in the polymerization to some extent. The IR analysis of a polymeric film, however, indicated the presence of some free carbonyl groups. The monomer in its molten form undergoes rapid photopolymerization in the presence of the methyl ether of benzoin. Benzoyl peroxide and N,N-dimethyl-p-toluidine, also initiate polymerization in a few minutes at 50°C.

Thermal polymerization of this monomer on a bone substrate resulted in, at first, a colorless film. However, on standing, the film became slightly yellow. A control experiment on a glass slide gave only a colorless film, which did not yellow with age. The development of the yellow color on bone may be due to reaction with free amino groups in the collagenous substrate via a Schiff base type of reaction. The film has resisted removal by soaking in acetone or water. A corresponding film on a glass slide was removable by solvent action. If these preliminary experiments are valid, this type of monomer may prove useful in improving adhesion to dentin and bone. We plan to investigate this monomer further and to synthesize liquid monomers with free aldehyde groups to augment this reaction with the collagenous substrate. Moreover, since aldehydes are oxidizable to carboxylic acids, the further possibility exists of improved adhesion through interaction with the mineral phase of the substrate, as well as through reaction with the collagenous phase.

A liquid aldehyde monomer of the aliphatic class has now been synthesized. It is derived from 5-hydroxypentanal by the appropriate condensation reaction with methacryloyl chloride.



$$CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-Cl+HOCH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}H\xrightarrow[CH_2Cl_2]{Et_3N}$$

$$CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}H$$

This monomer is a colorless liquid of moderate viscosity. Characterization of this functional monomer is in progress.

The polyfluoroaromatic methacrylate, 2-methacryloxyethoxypentafluorobenzene, has been successfully polymerized by chemical initiation (benzoyl peroxide). A sample of the homopolymer has been immersed in distilled water at room temperature in order to determine if this polymer has any fluoride ion releasing capability. The fluoride ion concentration will be measured periodically by means of a fluoride electrode.

Another interesting functional monomer which may have the ability to slowly release F^- after polymerization is that derived from the reaction of pentafluorophenol and 2-bromoethyl methacrylate in the presence of potassium carbonate in an aprotic solvent. The monomer is fluid despite its relatively high molecular weight (296). We hope to study the polymerization and copolymerization of this monomer and the behavior of the corresponding resins in water. The presence of any F^- will be determined, using the fluoride electrode method previously reported for the model compounds.

This, and similar fluoroaromatic monomers, may also react with free amino groups as well as H_2O present in collagenous substrate and thereby form covalent attachments while F^- is being released into the mineral phase.

D. Polymeric Grafting, A Technique for Bonding to Mineralized Collagen Surfaces

Grafting of polymeric side chains to hard tissues such as bone or dentin offers an attractive technique of altering the surface properties, especially the surface characteristics. It is a potential means to obtain good adhesion to hard tissue surfaces. Such techniques may find applications in improving adhesion of restorative materials to dentinal surfaces and as bone cements in oral surgical procedures.

Grafting of polymers to bone surfaces was continued using the persulfate-bisulfite redox system as initiator. As judged by weight gains of bone, 2-cyanoethyl acrylate, cellosolve, glycidyl methacrylates, and 1,3-butylene dimethacrylate were the most effective grafting agents. Moderate grafting yields were achieved with solutions of zinc or calcium acrylates, hydroxyethyl methacrylate, ethylene dimethacrylate and divinyl benzene. Little or no reaction occurred with a number of monomers such as 2-ethylhexyl acrylate, hexafluoroisopropyl acrylate, isobutyl methacrylate and pentadecafluorooctyl methacrylate.

A manuscript entitled "Chemical Modification of Hard Tissues - I. Bone" was prepared and submitted for NBS review. Additional experiments have been conducted to provide further evidence for some of the conclusions drawn in this paper.

A series of monomers of different chemical structure was evaluated for possible application in photopolymerization experiments designed to modify hard tissue either by grafting, interpenetration or adsorption onto the substrate.

In these experiments, a Nuva Seal light was employed. A number of photoinitiators were examined, but in most of the polymerizations, the methyl ether of benzoin was employed. Except in a few cases, most monofunctional monomers (e.g. methyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxyethyl methacrylate, styrene, benzyl acrylate, tetrahydrofurfuryl methacrylate, pentadecafluorooctyl methacrylate, methacrylic acid and 2-dimethylaminoethyl methacrylate) gave little, if any, polymer on glass microscope slides, even after prolonged irradiation (2 minutes). However, an equimolar mixture of the last 2 monomers, methacrylic acid and 2-dimethylaminoethyl methacrylate, produced a polymeric film in 30-40 seconds. Apparently, the two monomers act as a more viscous difunctional monomer because of H-bonding.

A second monofunctional monomer that formed a polymer in 30-40 seconds is the monoester derivative of 2-hydroxyethyl methacrylate and phthalic acid. Again, the monofunctional monomer acts as a difunctional one, probably due to H-bonding of the free carboxyl group. The polymer formed was a clear, hard film. This monomer will be evaluated for any adhesion-promoting ability due to the presence of the free carboxyl group which may interact with mineralized tissue or enamel. Preliminary experiments have indicated there is greater adhesion to enamel with this monomer system than with Bis-GMA.

Except for the exceptions noted above, most monofunctional monomers do not photopolymerize at a fast enough rate to be clinically applicable. It seems that the photopolymerizability of methacrylate monomers may be related to their functionality and viscosity. The more viscous difunctional methacrylates set up faster than the less viscous (e.g. Bis-GMA versus ethylene glycol dimethacrylate). The aromatic diester dimethacrylates, aromatic diether dimethacrylates and the aromatic ether-ester dimethacrylates, all polymerize nicely to tough, clear coatings. Since these monomers are not as viscous as Bis-GMA, they do not require the addition of a diluent comonomer (e.g. MMA).

In an attempt to obtain a more hydrophobic and oleophobic coating, equivalent amounts of triethylene glycol dimethacrylate and pentadecafluorooctyl methacrylate were photocopolymerized. Most of the polymerization occurred in the triethyleneglycol dimethacrylate layer and the polymer was not particularly hydrophobic. However, using chemical initiation, with N-N-dimethyl-p-toluidine in the highly fluorinated monomer and benzoyl peroxide in the triethyleneglycol dimethacrylate, a polymer was obtained with a more hydrophobic outer coating. We hope to apply this technique to make more water and oil-resistant sealants.

In addition to studying the photografting behavior of acrylate and methacrylate monomers, which may graft to collagenous substrates by free radical coupling reactions, we have explored the possibility of grafting via other chemical reactions by means of functional monomers. For example, it is well-known that collagen is capable of undergoing the Schiff base reaction with aldehydes. There are indications that the interesting functional monomer, 2-methacryloxyethoxybenzaldehyde, may be capable of forming covalent links with collagenous surfaces via the Schiff base reaction. Subsequent polymerization or, more likely, copolymerization with another methacrylate monomer should result in successful polymeric grafting.

Previously, we had shown that the solid monomer (m.p. 47-48°C), 2-methacryloxyethoxybenzaldehyde, could be polymerized in the molten state (approx. 50°C) by chemical or photoinitiation. On a collagenous surface such as bone, a tough, slightly yellowish, film was formed by thermal polymerization of this monomer, which was resistant to removal by organic solvents and water.

We have shown that it is possible to copolymerize a solution of this aldehyde methacrylate in methyl methacrylate by UV irradiation at room temperature. Work is in progress to evaluate the adhesive strength of such copolymers on collagenous substrates compared to similar polymers without the aldehyde monomer.

A liquid aldehyde methacrylate of the aliphatic class has been synthesized and will also be evaluated as an adhesion-promoting comonomer.

II. Physical, Mechanical and Physicochemical Properties of Hard and Soft Tissues and of Dental Materials

A. Dimensional Changes in Tooth Structure

The property of dimensional change of dental restorative materials relative to host tooth components is of obvious clinical importance. Presumably, differences in capacity for dimensional change should be minimized if problems such as marginal leakage are to be avoided. Differences may impose severe strains on interfacial bonding, thus severely inhibiting development and/or retention of adhesive bonding.

The dimensional changes of tooth enamel and dentin on heating and cooling are to a considerable extent governed by the thermal expansion of the mineral component of the tooth. However, particularly with dentin, the dimensional changes are modified by the organic component. Although collagen has a high coefficient of thermal expansion, its presence reduces the thermal expansion of dentin. Thus, it is evident that although the dimensional changes are induced by temperature change, other factors (such as changes in water content) are involved. Similarly, factors other than thermal expansion of components may be involved in the temperature-induced dimensional changes of restorative materials.

The objective is to determine the temperature-related dimensional changes of human tooth enamel and dentin and of restorative materials, to explain these changes in terms of various factors such as water content, micro and macrostructural aspects, phase changes, or degree of bonding of components which may be involved, and to point out possible relationships between thermally-induced dimensional changes and clinical performance of restorative materials.

Data obtained on the thermal expansion of enamel, whole dentin, anorganic dentin, bovine bone and bovine dentinal collagen and on the temperature-dependent changes in water content of bovine Achilles tendon, kangaroo tail tendon, ivory and seal tooth, provide a consistent picture of the thermally-dependent dimensional changes of tooth structures. In brief, the data indicate that the collagen component is responsible for the time-dependence of the thermal expansion of dentin. The dimensional changes of collagen resulting from its loss of water on heating (in water), and its gain of water on cooling, do apparently greatly affect the dimensions of dentin. Neither the thermal expansion of collagen nor its phase transformation dimensional changes appear to be major factors in the effect of collagen on the dimensional changes of dentin.

In dentin and bone, large anisotropic variations in the coefficient of linear thermal expansion are observed. (In bovine femur, for example, the coefficient was found to vary from near zero in the radial direction to approximately $2.5 \times 10^{-6}/°C$ in the circumferential direction, and approximately $8 \times 10^{-6}/°C$ in the axial direction. Measurements made along three mutually perpendicular axes in human tooth enamel indicate anisotropy. However, the directional variations are much less prominent than in dentin or bone and the data obtained so far do not relate the direction of minimum expansion to any specific direction within the tooth. The magnitude of the variations observed in enamel are shown in the table below:

Thermal Expansion of Tooth Enamel
10 to 60°C

Orientation Relative to Tooth Surface	Coefficient X 10^6			
	Spec A		Spec B	
	Coef.	S.D.	Coef.	S.D.
Perpendicular	13.0	0.3	11.7	1.0
Parallel	11.8	0.5	13.4	0.2
Parallel	13.1	0.5	13.4	0.2
Volume Expansion	37.9		38.5	

If it is assumed that in the specimens used for these measurements, the enamel rods are approximately perpendicular to the tooth surface, no relationship between rod direction and coefficient of thermal expansion is apparent. However, a precise determination (not yet made) of rod orientation within the specimens may show more correlation than is now evident.

B. Wear Resistance of Dental Restorative Materials

The property of resistance to wear can be assumed to be a critical one for all dental materials subject to any of the various types of wearing forces in the mouth. It is, of course, crucial for materials placed at occlusal surfaces where stress is imposed. Development of adequately wear-resistant materials, without degrading other properties, would be greatly assisted by design of a laboratory system which could simulate clinical wear performance. To be of practical value, the laboratory system should reduce by several orders of magnitude the time required to observe measurable (and reproducible) quantities of wear. The problem is thus the selection and incorporation of the optimum combination of mouth-simulation, accelerating and variable-reducing characteristics. Once this has been accomplished, the system can be used to determine wear characteristics of materials before they are subjected to extensive clinical evaluation.

The initial design and construction of a simulated physiological wear generating and measuring device (Figure IIB-1) were given in detail in the FY 1975 Annual Report. The wear generating portion of the device has posed no problem; however, modifications to the measuring, and later to the data collecting, systems have been necessary. Measurements have been restricted to one commercial amalgam and one commercial composite, each of which have been the subject of one, two, and three-year clinical observations.(11-13)

Due to the apparently erratic nature of some of the wear depth measurements, improvements were made toward stability. These include: (1) a solenoid operated water shutoff valve to prevent flow of water over the measuring points and beam ends while they are in their down (measuring) position; (2) blunting of the wear track measuring pointer to prevent its falling into small voids or grooves in the bottom of the wear track; (3) an improved relay coil power supply to the drive motor braking system to provide greater reliability in placing the measuring points in the same spot for each measuring cycle; (4) factory reconditioning and updating of the recorder for wear depth and fluid environment temperature; and (5) addition of a voltage regulating power supply to the LVDT signal conditioning module to eliminate the possible effect of line voltage surges.

Initial testing of a very limited number of specimens showed a marked difference between the wear resistance of an amalgam alloy and a composite restorative material in the same order of wear shown by prior clinical service testing.

Referring to the volumetric wear equation:(14)

$$V = \frac{kWL}{3p} \qquad (1)$$

V = Wear volume (in mm^3)
k = Wear constant
W = System load
L = Length of slide (total)
p = Penetration hardness of softer wear couple member

the wear constant k has been described as a statistical probability that a fragment of wear debris will form between surface asperities of materials in sliding contact.(15) It is analogous to coefficient of friction and is generally referred to as the coefficient of wear. Consequently, it is a very convenient term used to describe the wear performance of materials in a sliding mode. It must be remembered, however, that materials for which these concepts were developed may have vastly different properties from those of concern in this investigation. Smaller coefficients of wear (k) values indicate greater resistance to wear.

To arrive at the wear coefficients, a straight line was fitted to the recorded wear track depth data to give a least-square estimated slope on a wear vs. time plot for the two materials tested. Calculated depth of wear values for each 10-minute running period between measurements were .0304 μm for the amalgam, and .0743 μm for composite restorative material with standard errors of the slopes of .0109 and .0238, based on 34 and 25 measuring points, respectively.

As observed in the statistical information, the standard errors of slope left something to be desired in that the slopes were different only at a 90% level of confidence, using the significance test described by Bowen and Argentar.(7) Further examination, however, indicated that, with a capability of testing for a 24-hour run, the precision of slopes could be improved by approximately 2.5 times:

$$\begin{array}{l} \text{degrees of freedom 24-hour run} = 142 \\ \text{degrees of freedom present run} = \ \ 23 \end{array} \qquad \sqrt{\frac{142}{23}} = 2.5$$

In order to test for the longer period, it was necessary to improve the fluid supply to the testing apparatus.

A 75-liter shaker bath was procured, modified and installed with the testing apparatus. The bath was connected directly to the facility distilled water supply through a regulating float valve and provides a continuous supply of 37°C (± 1°C) distilled water to the test specimen. The water temperature has proved sufficiently stable that the thermocouple output recording was discontinued.

A modification was also made regarding the electrical circuit responsible for stopping the restorative specimen under the depth measuring tips. Additional circuitry allowed two points on the wear track (180° apart) to be measured instead of one, and, in effect, doubled the original data output for each restorative specimen. The two points were measured alternately after each 20-minute wear period.

In an effort to expedite testing time, five specimens each of an amalgam and a composite restorative material were tested under a load of 1.5 kg/mm^2 of enamel face contact instead of the original 1 kg/mm^2. Unfortunately, the 1.5 kg/mm^2 load proved too high for the amalgam-enamel couples, causing edge fracture of the enamel sliders. The sharp fractured edges exercised a milling effect under sliding and removed far more restorative material than normal from the wear track, falsifying the wear data. As a result of these findings, all future tests of this configuration were limited to 1 kg/mm^2 loads.

Wear coefficients were calculated from test volumes using the Archard equation (Eq. 1). Coefficients were also calculated using the equation used by McGrew(16) (Eq. 2):

$$V = KmWL \qquad (2)$$

$$Km = \text{Wear coefficient without hardness influence}$$

These K values differ from the original Archard equation values in that these are given in units of mm^3/mm kg, based on wear volume divided by sliding distance and by load. The difference between the two methods of calculation is in the use of hardness values. In the Archard equation, the quotient derived by the division of the product of load and sliding distance into the wear volume is multiplied by three times the hardness value for the material tested. The McGrew equation omits any consideration of hardness.

Observation of alternately recorded points on the analog strip chart showed a depth differential between the two sets of measured points. While some differential (5-6 μm) may be expected from loss of perpendicularity to the vertical mounting position due to the pretest preparation and polishing of specimen surfaces, the amount observed ran as high as 18 μm. Also observed was the fact that the rate of wear measured at the two positions was seldom similar. From the observations, it was concluded that the 360° wear track may not be of uniform depth; probably a consequence of dissimilar wear rates at various locations around the wear track. It is possible that the nonhomogeneity of restorative materials throughout their bulk could account for dissimilar wear rates at their wearing surfaces. Such an occurrence has not been previously reported in dental materials literature.

The non-uniformity of track depth was confirmed by multiple surface profile measurements made with a Talysurf profilometer moving from the unworn material inside the wear track circle, across the track to unworn material outside the circle (Figure IIB-2). Comparison of the various track crossings on the same specimen indicated track depth differences as high as 15 μm. Considering that the previously indicated wear for the total test run was based on the average of the two measured depth points, it was concluded that only two measuring points on the wear track would not be sufficient for precise total wear track volume measurements.

It was decided that a minimum of ten measured points, equally spaced around the 360° wear track, would produce the desired precision. While the two measuring periods per hour could be handled easily, the greatly increased data acquisition rate from 10 points would render the data recording method highly impractical.

In order to efficiently collect and prepare for computer processing the large amount of data generated, an integrated data acquisition system was procured on loan from the Microcalorimetry Section and the ADA. The system consists of a digital voltmeter with binary code digital output to receive the calibrated depth measurements from the measuring tip-LVDT system. The voltmeter is interfaced through a coupler-controller to a teletype equipped with a paper tape punch. The teletype provides a direct printout of data as well as punched data-containing tape in American Standard Code II for direct input to computer processing (Figure IIB-2).

In order to provide ten equally spaced depth readings taken at the same relative point on the specimen for each measuring cycle, a triggering device was required. A ten-slot chopper wheel was constructed and attached to the specimen turntable shaft. A light source-photocell receiver-amplifier device was designed and constructed and saddled over the edge of the chopper wheel. The purpose of this device is to command the data acquisition system to take a single measurement each time light is admitted by a chopper wheel slot.

After each thirty-minute wearing period, the specimen turntable is placed into one slow (15-second) revolution during which time the sapphire tipped measuring points are in contact with the wear track and reference area. During the 15-second revolution, the ten-slot wheel initiates the digital voltmeter to effect the recording of ten equally spaced wear track depth measurements and the current time of day on the teletype printout and placement of the data on punched tape.

Data from the ten-point measuring system has verified the suspected inaccuracy in the old one and two-point system. The average wear coefficient for the ten measured positions of the latest measuring system gives values of 0.45×10^{-4} and 0.46×10^{-4} for the same materials above. These last two figures do not actually suggest the same wear resistance for both materials as it may appear. It must be remembered that the values were derived from the Archard equation (Eq. 1) in which K (wear coefficient) is directly proportional to hardness. The wear coefficient values for the same two materials as calculated from the equation as taken from McGrew (Eq. 2) are not influenced by hardness. These k_m values were found to be 0.22×10^{-6} and 0.13×10^{-6} mm^3/mm kg for composite and amalgam, respectively. The validity of these latter k_m values is reinforced by the average volume loss per minute per square millimeter of wear couple contact which were 0.23×10^{-3} and 0.13×10^{-3} $mm^3/min(mm^2)$ for composite and amalgam.

For data treatment, two statistical models were used. In the first model, the errors were assumed to accumulate with the passage of time as wear occurs. The second, or independent mode, has been shown to be useful in a number of experimental instances where a specimen undergoes change with time and a property affected by the change in the material is intermittently measured.

Results so far obtained are consistent with the assumption that the true error model lies somewhere between the independent and the cumulative with composites favoring the independent and amalgam the cumulative model. Techniques for handling such cases have not heretofore been published.

Some of the sources of variability in the data are shown in the next few Figures. Figure IIB-3 shows a plot of wear-track depth versus time. Each point is an average of the ten depth readings taken at the end of a 30-minute wear cycle. The data for the composite show a fairly uniform wear pattern. There are some apparent reversals in depth, but they seldom represent more than a few tenths of a micrometer. The curve for amalgam, while it shows a lower average wear rate, is also more irregular. The pattern of alternating slow and rapid wear seems to be typical of amalgam. Transfer of amalgam to the surface of the enamel slider occurs during the wear period. Whether or not the fluctuations in wear rate correspond to fluctuations in the amount of amalgam on the slider has not been determined, but that would appear to be a possibility. The data indicate the necessity for testing over a long wear period since wear rates based on short periods could vary greatly.

Figure IIB-4 shows for amalgam the variation of depth of wear at the ten measurement positions around the approximately 40 mm circumference track. Each of the curves connects ten depth measurements made in the course of one measurement cycle. It is obvious that some areas of the specimen show more wear than do others. Also, as indicated by the similarity of the curves obtained at different times, the wear patterns established during the first few hours of the test period tend to continue throughout the period. Thus, it appears that there are variations in wear resistance throughout the specimen, and the average value for a particular specimen will depend on the mix of low and high resistance areas in that specimen.

Figure IIB-5 shows that the variation in wear resistance from one position to another occurs in the composite as it does in amalgam.

One anticipated source of scatter in the wear results was the variability of sliders made from human enamel. It was thought, however, that the use of enamel with its inherent variability offers advantages over other materials which might be more uniform, but would not duplicate the wear characteristics of enamel. It is difficult to determine the contribution that differences in the enamel make to the variability of the results since sliders often cannot be used for more than one test period. Even when a slider can be re-used, there is the possibility of different wear characteristics at different depths in the enamel. Examination of several sliders after use indicated that there were significant deviations from the intended orientation of the enamel rods perpendicular to the wear surface. More uniform preparations may reduce the scatter in future measurements. We would like to substitute another material for the enamel, but at present we do not know of a material which satisfactorily duplicates the characteristics of enamel as the antagonist in the wear couple.

Although this study has not included measurements of the volume loss of enamel, it is obvious that enamel loss is much greater when sliding in contact with the composite material than when against amalgam. This observation, which is in agreement with results reported by Powell, Phillips and Norman,(17) may have clinical significance no less important than that of the wear rates of the restorative materials.

The results reported herein were presented before the American Association for Dental Research meeting in New York, April 1975.(18)

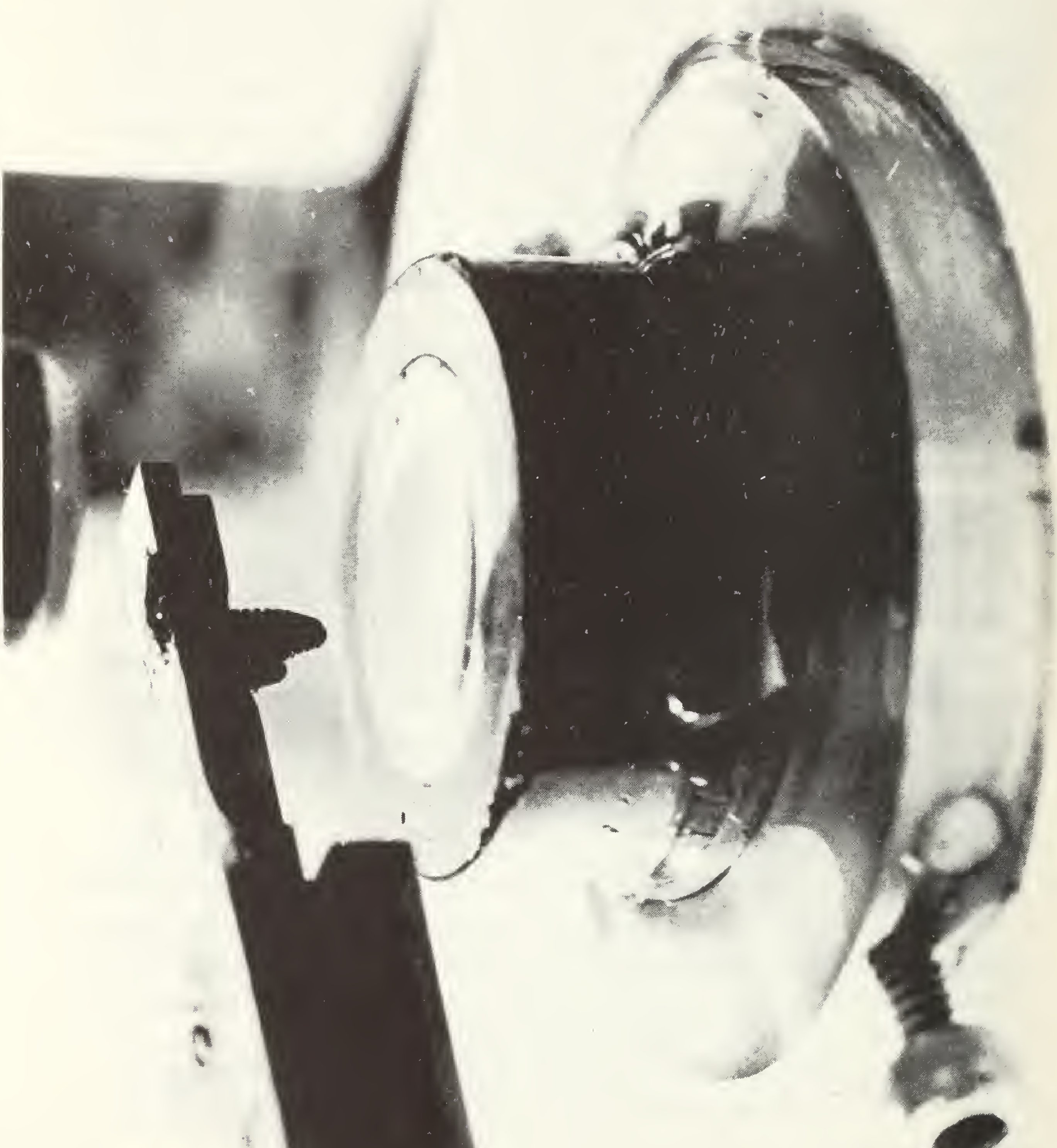


Figure IIB-1

DATA ACQUISITION SYSTEM

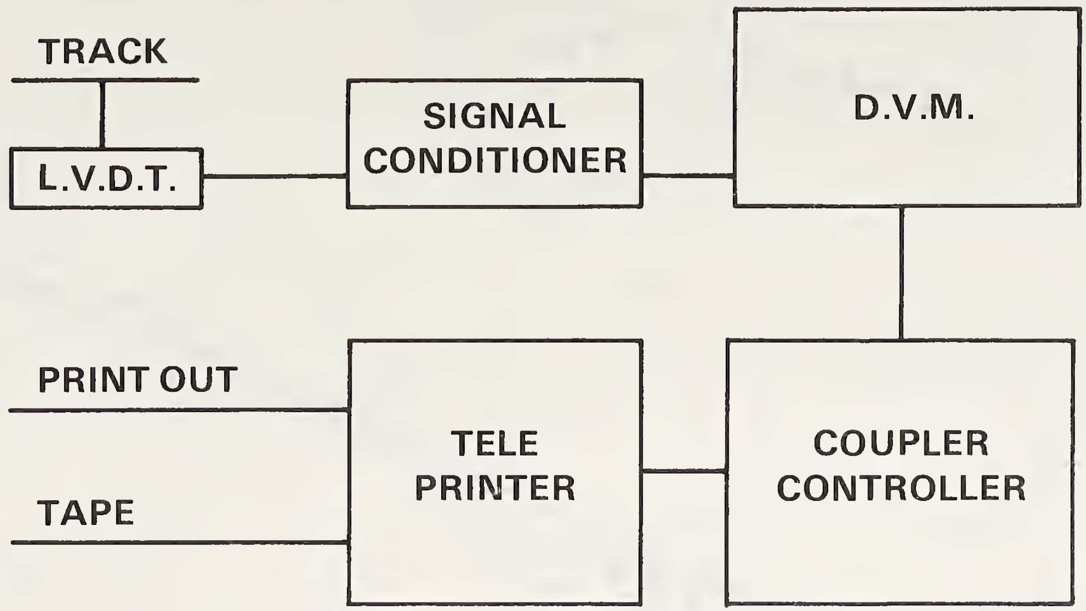


Figure IIB-2

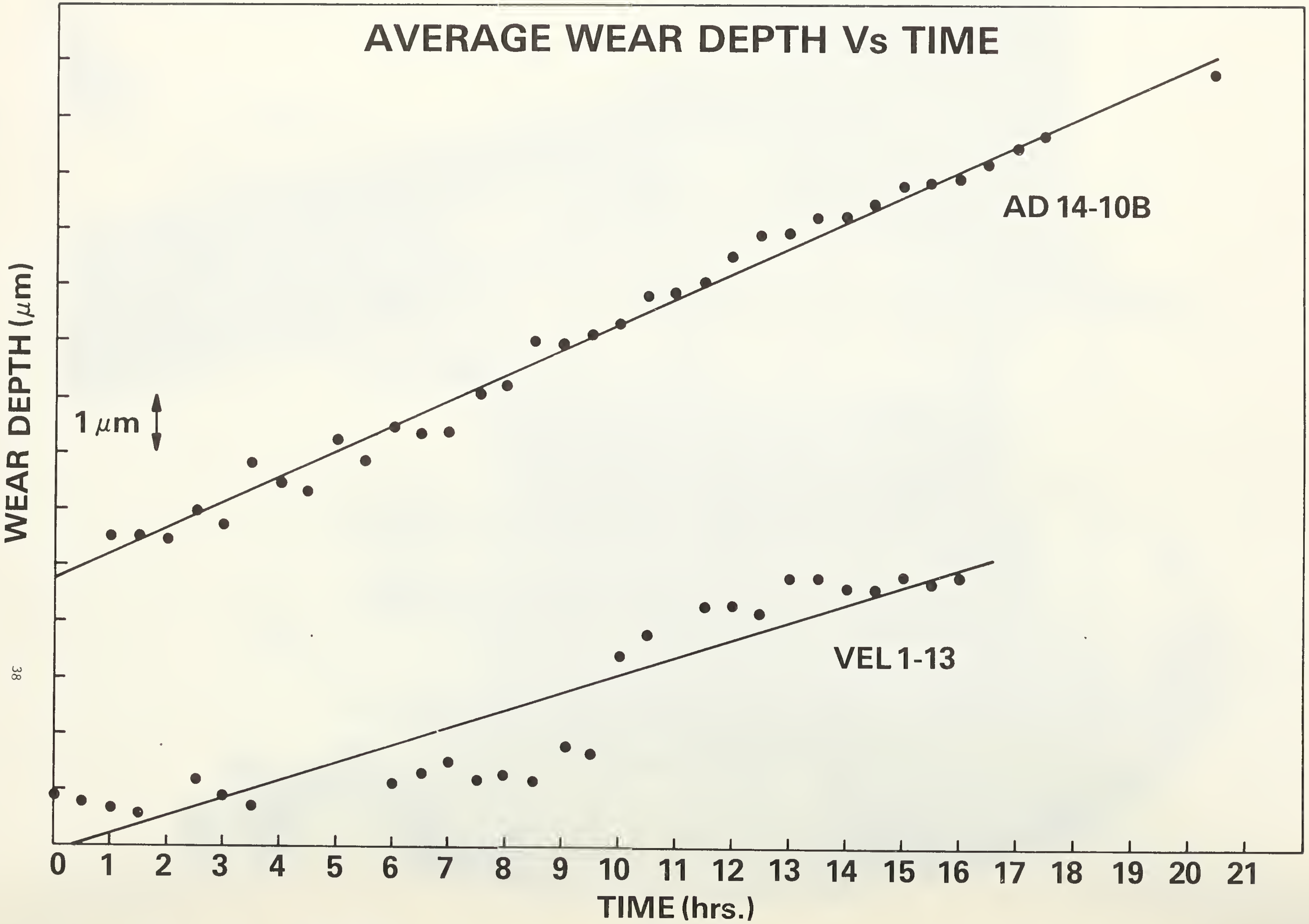

AVERAGE WEAR DEPTH Vs TIME
WEAR DEPTH (μm)
1 μm
AD 14-10B
VEL 1-13
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
TIME (hrs.)

Figure IIB-3

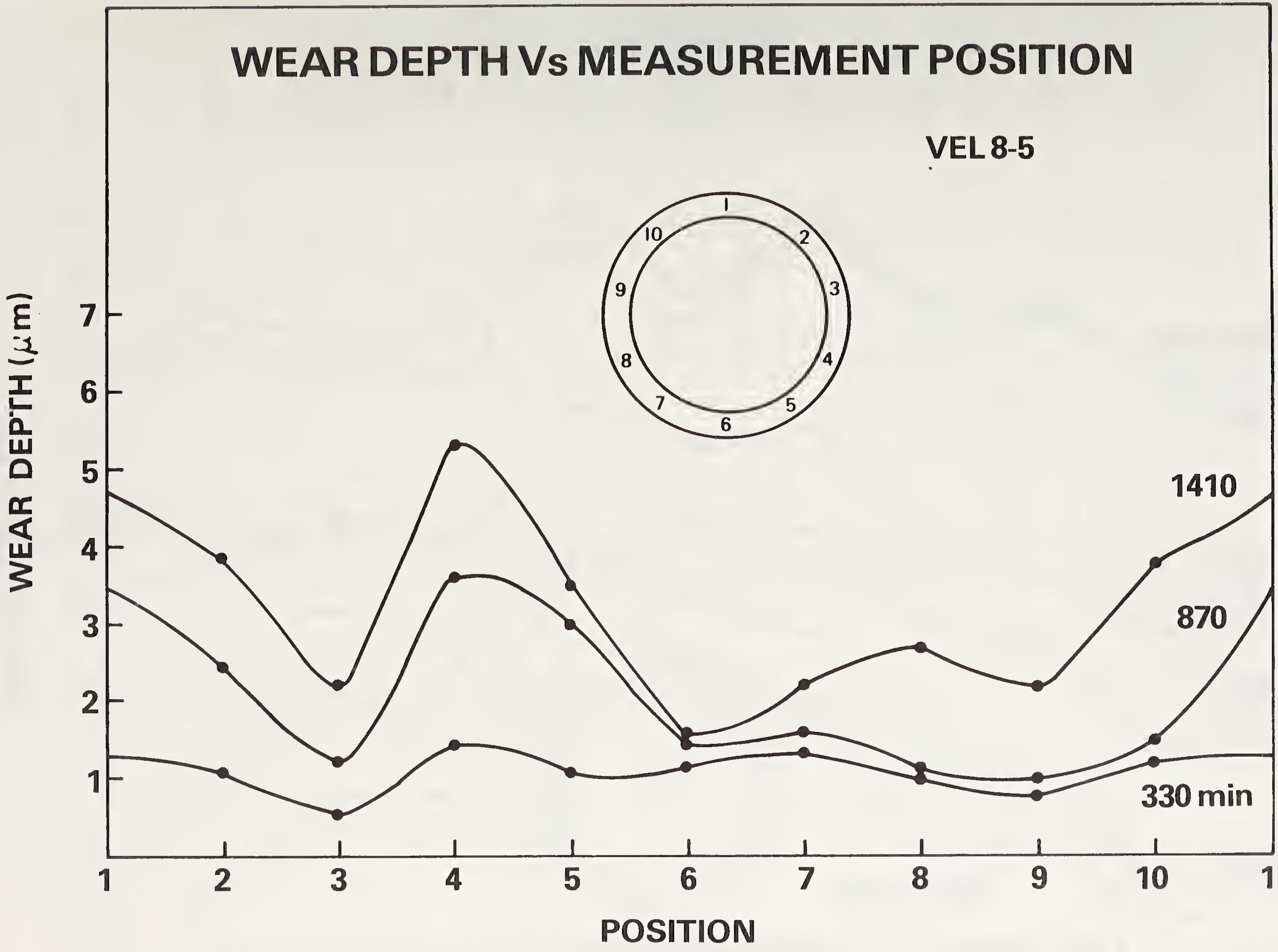

WEAR DEPTH Vs MEASUREMENT POSITION
VEL 8-5
1
2
3
4
5
6
7
8
9
10
WEAR DEPTH (μm)
7
6
5
4
3
2
1
1410
870
330 min
1
2
3
4
5
6
7
8
9
10
1
POSITION

Figure IIB-4

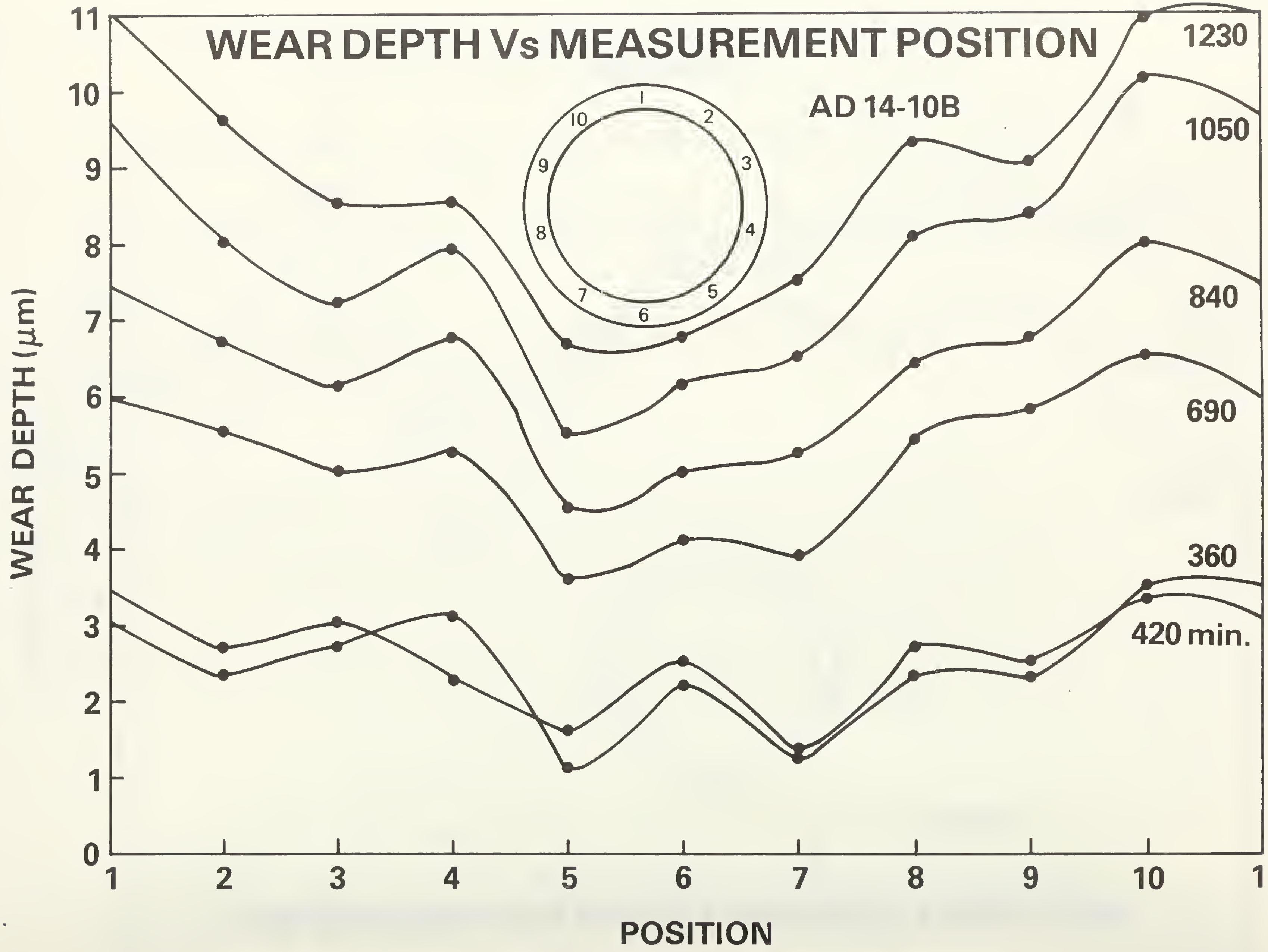

WEAR DEPTH Vs MEASUREMENT POSITION
AD 14-10B
WEAR DEPTH (μm)
11
10
9
8
7
6
5
4
3
2
1
0
POSITION
1
2
3
4
5
6
7
8
9
10
1
1230
1050
840
690
360
420 min.
1
2
3
4
5
6
7
8
9
10

Figure IIB-5

C. High Modulus Reinforcement, Techniques for the Improvement of Dental Cements and Composites

The objective of this research is to develop techniques for improving the interfacial bonding between the reinforcing filler and the polymeric matrix of dental cements and composites. Initially, our efforts have been directed toward improving the properties of dental cements of the polycarboxylate type. If successful, these studies would be extended to other dental composite systems.

Since the polymeric matrix of the polycarboxylate cement is basically poly(acrylic acid), we have attempted to make the reinforcing filler component more compatible with the matrix by depositing a thin coating of the same or a similar polymer on the filler particles. Ideally, to achieve strong interfacial bonding, the polymeric coating should be firmly attached to the filler particles as well as being chemically and physically compatible with the polymeric matrix.

In the present study, a commercially available polycarboxylate (PCA) provides the polymeric matrix of the cement. Two fibrous materials, potassium titanate and graphite, have been selected as reinforcing fillers.

Several techniques for the deposition of thin polymeric coatings onto the filler particles are under evaluation.

One technique involves allowing monomer in the vapor state to permeate the filler in a vacuum. The monomer is subsequently polymerized in situ. Our initial attempts at using this technique have involved the use of acrylic acid as the monomer, and gamma irradiation to initiate polymerization. Some problems were encountered using this technique, primarily having to do with polymerization of the monomer prior to deposition on the filler particles. However, a crude burning test of each treated fiber indicated the presence of some polymeric deposit. The acidity of aqueous suspensions of the two treated fibrous fillers was found to range from pH 3.3 - 3.9. An equilibrated aqueous slurry of untreated potassium titanate had a somewhat basic pH of 8.5. The untreated graphite suspension was virtually neutral. Extraction of the treated fibers with water for 24 hours (Soxhlet extraction) removed some of the poly(acrylic acid) deposit (pH of extract reached 4.0 - 4.6). A further extraction with dioxane (a good solvent for poly(acrylic acid)) removed virtually all of the coating from the graphite (pH 5.3), but had little effect on the potassium titanate fibers (pH 4.6). It would appear that some acrylic acid and/or poly(acrylic acid) has become ionically attached to the potassium titanate, perhaps because of the somewhat basic character of this filler.

A second technique for polymer deposition onto filler is to suspend the filler in a dilute solution of monomer and evaporate the solvent with constant agitation. The monomer, coated on the filler particles, may be polymerized by thermal and/or chemical initiation. We have used this technique to prepare potassium titanate fibers coated with the polymer of the acryloxyethyl ester of phthalic acid ($CH_2 = CHCO_2CH_2CH_2O_2CC_6H_4CO_2H$). Polymerization of the monomer was achieved by simple thermal polymerization under vacuum.

A related technique involves the deposition of polymer from a polymer solution onto the filler. For example, potassium titanate fibers were agitated in a dilute aqueous solution of polyacrylic acid while the solvent was gradually stripped away under vacuum. A comparison of these treated fibers with those obtained from the gamma radiation polymerization of vaporized acrylic will be made.

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

A diversity of experimental approaches is being investigated to develop techniques which can be applied in formulation of adhesive restorative and caries-preventive dental materials. A newly developed testing procedure, still in the evaluation stage, has demonstrated expected ranking of adhesive bond strengths within a group of selected coating agents, both coupling and release types. Deterioration on exposure to water of cohesive bond strength in the Bis-GMA matrix has been indicated without concurrent deterioration of the coupling agent. A monomer system with potential as a composite or pit and fissure sealant resin and giving a polymerizable liquid of desired viscosity at room temperature was derived from three low-melting, crystalline isomers of ether-ester linked aromatic dimethacrylates. A series of monomers of varying chemical structure was evaluated for possible application in photopolymerization experiments designed to investigate modification of hard tissue by grafting. Modifications to extend the running time of a dental restorative wear-generating experiment three-fold and which allow the computerized recording of ten, instead of two, depth of wear measurements around the circular wear track have significantly reduced the standard error of measurement. Surface coating techniques being developed to strengthen interfacial bonding in dental cements and other dental materials show more promise with titanate than with carbon reinforcing fibers.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Adhesive materials; composites; dental materials; polymer grafting; resins; restorative materials; sealants; wear resistance.

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