NBSIR 81-2431

Properties and Interactions of Oral Structures and Restorative Materials

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Materials Science
Polymer Science and Standards Division
Dental and Medical Materials
Washington, DC 20234

Annual Report for Period
October 1, 1980 thru September 30, 1981

Issued December 1981

Interagency Agreement
YOI-DE-40015-11

Prepared for
National Institute of Dental Research
Bethesda, MD 20014

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, ***Secretary***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

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ABSTRACT

Significant accomplishments in the field of dental materials research for the past year include:

(1) New dental cements, based on esters of vanillic acid or its isomers, that overcome major shortcomings of zinc oxide-eugenol cements have been formulated. Noninhibition of the polymerization of dental methacrylate resins that they contact, along with improved strength and solubility properties are advantages gained with the new materials.

(2) A Fourier Transform IR spectroscopic examination of the cyanoacrylate-purified collagen (dry) interaction indicates that the high initial bond strength of cyanoacrylates to dentin is accomplished through secondary bond formation which by nature will tend in time to be broken by water.

(3) A very close relationship was demonstrated between the softening of composites by chemical solvents selected for food simulation and composite wear performance as measured with a classical pin (stainless steel) on disc (composite) wear apparatus. A correlation was demonstrated between wear, after immersion of the composites in ethanol/water solutions, and the change in hardness of the composite resin during its immersion.

(4) Thin section, optical, transmission microscopy, applied to clinically worn composites after silver staining for contrast, revealed that defects within the damaged sublayer beneath the wearing surface were distributed throughout the polymer matrix rather than confined to the filler/matrix interface.

(5) A theoretical development of small angle x-ray scattering (SAXS) as applied to three phase (filler, matrix, microcrack) systems permitted the volume concentration and characteristic length of microcracks in both _in vitro_ and _in vivo_ worn composite specimens to be determined.

(6) Theoretical calculations showed that for the porcelain/alloy thickness ratios (i.e., $\geqq 1$) being employed experimentally, interfacial effects could be neglected for the split ring gap change analysis and a knowledge of a precise value for Poisson's ratio was not required.

SUMMARY

Efforts to provide resin systems for composites that shrink minimally on polymerization demonstrated that composites with good properties could be obtained using the very bulky diurea dimethacrylate reaction product of N-t-butyl-2-aminoethyl methacrylate and hexamethylene diisocyanate. Similarly we have demonstrated useful composite formulations employing a bulky monofunctional tricylic aliphatic methacrylate. To produce hydrophobic BIS-GMA type monomers we have reacted highly fluorinated alcohols with diepoxy compounds to produce diols that in turn are convertible to diacrylate monomers as desired. Initial results with bulky polythiols, i.e., $R(CH_2-SH)_x$ with $x \geqq 2$ indicate that these compounds may be useful with non-amine accelerated systems as well as with the conventional amine-peroxide type.

Three amines, p-(dimethylamino) phenethanol, p-(diethylamino) phenyl acetic acid and its ethyl ester, shown previously to be promising fast acting accelerators for dental composites, were synthesized in greater quantities and offered to cooperating laboratories to determine their toxicological and biocompatible characteristics. The p-(dimethylamino) phenethanol, synthesized and evaluated in this laboratory is now available from a chemical manufacturer.

Some promising leads have developed for improving the storage stability of initiator-accelerator components of composite formulations where the non-amine accelerator, ascorbyl palmitate (AP) is employed. This promising accelerator creates no storage stability problems in powder-liquid formulations when it is coated on the surface of the powder. By employing a combination of bisulfite and dihydroxymaleic acid we have retained the original setting time after three months in formulations where AP is dissolved in the monomer for paste/paste application.

A non-spectroscopic method, differential scanning calorimetry (DSC), has been demonstrated to be a useful additional tool for assessing the extent of polymerization (EP) in dental resin systems. Since the EP is a major controlling factor in developing the properties of the polymerizing system and because traditional IR analytical methods may be hampered by strong interference in the vinyl absorption region, the demonstration that DSC offers a comparatively facile and rapid measurement for EP as well as a technique for determining the effectiveness of inhibitors should be of interest to composite resin developers.

Primary amines were shown to be the most effective, aromatic and heterocyclic amines the least effective, as catalysts for the silane coupling agent treatment of composite filler particles. Incorporation of one fluorinated silane agent into the normal silane coupling treatment of filler particles did not reduce water sorption of the resulting composites to the extent expected but indicated a potential means for gaining a whiter composite with better color stability.

A new dental cement has been formulated that overcomes a major shortcoming of zinc oxide-eugenol cements. The cements, based on esters of vanillic acid or its isomers, do not inhibit the polymerization of composite or resin formulations placed in contact as do zinc oxide-eugenol cements. Significant further advantages are evidenced by the strength and decreased rate of disintegration in water. Because of the potential usefulness of these new cement formulations a "patent disclosure" has been prepared.

To capitalize on the Guest Worker participation of Dr. Derrick Beech, Director of the Australian Dental Standards Laboratory and internationally recognized for his work on development of adhesive techniques for dental application, various mineralization pretreatments of dentin and the mechanisms governing the interaction of cyanoacrylates with dentin surfaces have been intensively examined. Results point to the importance of the role of cement-containing cations in the bonding of polycarboxylate cements to dentin. Calcium when precipitated on dentin as calcium phosphate ($(Ca_3PO_4)_2$) was shown to give significant improvement to the bonding achieved with either of the commercial polycarboxylate cements that were examined. Other precipitated metal phosphates generally produced a slight decrease in bond strength with a cement containing Sn^{++} or Zn^{++} ions. The latter ion as the cation of precipitated phospate is as effective as Ca^{++} while Sn^{++} has little effect. If Sn^{++} is not present in the polycarboxylate cement, Sn^{++} on the tooth surface many diffuse into the cement with concomitant loss of beneficial effects.

Fourier Transform infrared spectroscopy did not reveal evidence of any new bond formation when α cyanoacrylates were mixed with purified dry collagen. This evidence for a lack of primary bonding, combined with the instability to water of the initially strongly adhering cyanoacrylate-dentin interface, suggested the following explanation for this interaction: cyanoacrylates polymerize rapidly by initiation at the tooth surface (good adaptation, intimate contact); polymerize only in thin films (minimal polymerization stresses) and are very polar polymers (hydrogen bonding and dipole interactions with the collagen of dentin). Further, if adhesion is via secondary bonding only, then the deterioration of this bonding by water will not be affected by improving the resistance of the polymer to degradation.

Significant progress has been made toward the objective to develop, or make use of, appropriate techniques to measure wear resistance and mechanical properties of dental materials and to use the data obtained as performance indicators to predict in vivo durability of composite restorations. A classical pin on disc apparatus and an erosion technique provided basic information relevant and possibly essential to the development of an appropriate durability test. Complementary efforts involved microdefect analysis using x-ray and optical microscopic observation of damaged regions made resolute by a silver staining technique. It is asserted that for development of a relevant wear test, the subsurface damage resulting from in vitro wear should resemble that obtained from in vivo worn specimens.

A procedure for very careful calibration of the pin-on-disc apparatus has been developed that allows more precise interpretation of the data. A similarity in the results with dental composites to that experienced elsewhere with ultra high molecular weight polyethylene (the very durable plastic component of orthopedic prostheses) has been noted in that distinct regions of wear phenomena were evidenced by significant changes in the slopes of track depths (volume losses) vs track length or time of test. The initial relatively slow wear rate period, interpreted as being dominated by adhesion and/or abrasion mechanisms, was followed by an increase in subsurface damage to the point where severe breakdown occurs from fatigue. The occurence of the onset of a fatigue mode in the wear process has occurred at earlier times as the stress levels applied in the test were increased. Silver staining microdefect analysis of specimens removed from the wear process at the different stages of wear revealed essentially no subsurface damage in the initial (adhesive and/or abrasive) wear region but a considerable damage in the region where the fatigue mode of deterioration has been added to the wear process.

A very close relationship was shown between the softening of composites by chemical solvents selected for food simulation and their wear performance. The solubility parameters (Hildebrand theory) of various solvents

and BIS-GMA have been determined. The unfilled polymer is shown to have a solubility parameter with components $7 < \delta_d \leqq 9$ and $2 \geqq \delta_a \leqq 16$, the wide spread range of δ_a being attributed to the complexity of the chemical structure of this monomer molecule. The parameters δ_d and δ_a are the dispersion and the association components of the solubility parameter respectively, the units of these parameters are in $(\mathrm{cal/cm}^3)^{\frac{1}{2}}$. Measurements of Knoop Hardness and initial wear data e.g., track depths after only five cycles, showed that significant attack of BIS-GMA occurred in ethanol/water solutions as well as in pure ethanol. In fact the degradative effect as judged by initial wear data was significantly greater for a concentration of 75 percent ethanol in water than for 100 percent ethanol. The reversal in the order of the rates of wear at much longer time periods is attributed to differences in rates of diffusion of the immersion media. A correlation was obtained between wear, after immersion of the composite specimens in different ethanol/water solutions, and the change in hardness (KHN) of BIS-GMA as a result of similar immersion. Although the dependence of both wear and hardness rates were not monotonic with concentration, the dependence of wear on the hardness ratio is monotonic. Preliminary results with a visible light cured composite indicate that while its surface hardness decreased as the concentration of ethanol in water increased, the wear resistance remained good in contrast to the conventionally cured composites used as control.

A strontium glass containing composite was found to be much more susceptible to surface deterioration by acids than composites with conventional quartz or glass filler. Thermocycling did not significantly influence the physical properties of any of the composites.

Thin section, optical transmission microscopy of clinically worn composites, silver stained for contrast, revealed that defects within the damaged sublayer beneath the wearing surfaces were located throughout the polymer matrix rather than being confined at the filler/matrix interfaces.

A theoretical treatment of small angle x-ray scattering (SAXS) applied to three phase (filler, matrix and microcrack) composite systems was completed for presentation to an American Physical Society and IUPAC meetings in 1982. By SAXS analysis the volume concentration and characteristic length of the microcracks in the damaged sublayer regions of compression-fatigued, in vitro specimens differed from that of specimens recovered after clinical use.

The lack of fundamental knowledge regarding nonprecious and low precious metal alloys as alternatives to gold alloys for fixed partial dentures, has resulted in problems encountered clinically and in the dental laboratory. These problems have dictated the need for examination of the many factors involved, particularly in the porcelain fused to metal application. Residual stress in porcelain from cooling after firing is considered a primary factor leading to failures in the porcelain to metal bonding; precise universally agreed-to techniques for assessing porcelain/alloy compatibility do not yet exist. As a first step toward assessing compatibility and as a technique which might find acceptance as a standard method of evaluation, the analysis of gap changes in a porcelain veneered split metal ring subjected to laboratory firing schedules has continued. Theoretical calculations showed that the knowledge of a precise value for Poisson's ratio is not critical to either evaluation of stress or correlation of theoretically predicted gap changes with those determined experimentally. Calculated residual stress is, however, very dependent on the elastic modulus value and its determination for different porcelains is being planned for. Analysis showed quite clearly that no one-to-one correspondence in magnitudes or locations of maximum shear, tensile (compressive), tangential and radial stresses exist; this is important in consideration of stress relaxation and changes of the glass transition temperature as affected by cooling and stress.

The sensitivity of experimental measurements of split ring gap change to changes in properties of the procelain-metal interface was addressed. A theoretical study showed that while the porcelain/alloy thickness ratios being employed experimentally, i.e., $t_{porcelain}/t_{alloy} \geqq 1$, interfacial effects could be neglected, there are other conditions where this is not so.

A prime property needed for theoretical analysis of the split ring gap change is the temperature dependence of the shear viscosity (for stress relaxation/retention near Tg). This property was determined for several dental body porcelains. Although the viscosity itself was not measured directly, a close correlation was found between the strain point (found by others) and the temperature (obtained upon heating) of maximum rate of recovery of quenched excess volume for previously, rapidly cooled expansion specimens.

Studies were initiated to determine how precisely heat transfer properties are needed and to investigate other properties that may be deemed necessary for the complete analysis of split ring gap changes.

Much proposed testing of porcelain/alloy bond strengths utilizes testing of shear properties whereas failure is best reflected in tensile properties. Further, preparation of specimens for shear testing is often time consuming. A test is under development that utilizes the principle of developing uniform tensile stresses in layers of a uniform cross-section beam subjected to pure bending. The ease of specimen preparation and the non-sensitivity of results to porcelain thickness render the test design and methodology potentially attractive as a generalized adhesive bonding test.

Further development of castability test procedure employing a polyester grid pattern for determining an alloy castability value, CV, occurred (the percentage of completed cast segments is referred to as the castability value, CV). Preliminary results indicate that the optimum casting temperature (superheat) and mold temperature obtained by this method can differ from the manufacturer's instructions. Optimum casting conditions are accompanied by higher precision (predictability i.e., smaller standard deviation) for the CV.

A prime consideration in casting of dental alloys involves obtaining a satisfactory clinical fit of multiple unit, fixed, partial dentures (FPD's). This is of particular concern for nonprecious alloys which as a class are more difficult to join single units together by soldering. A study on factors affecting fit showed quite clearly that the use of an all wax spruing-runner bar system produced less distortion (better fit) than a pattern which is comprised of mixed materials, in wax and plastic.

INTRODUCTION

The National Bureau of Standards is primarily a measurement organization. Paths for 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, to commerical production by industry.

The dental research program at NBS is a cooperative effort both in personnel and funding, involving the American Dental Association and the U. S. Army and Navy Medical R&D Commands. With the exception of the research on porcelain fused to base metal alloy--research also participated in and partially funded by the U. S. Navy Medical R&D--the research described herein is only that portion of the dental program supported by interagency agreement with the National Institute of Dental Research.

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 materials used or potentially of use in restorative and preventive dental practices. The four major areas of research as approved in the interagency agreement are given below:

I. Dental Composite, Resin, Sealant and Cement Chemistry and Development

II. Development of Adhesive Bonding Techniques

III. Wear Resistance and Mechanical Properties of Dental Composite Restorative Materials

IV. Dental Alloys and Ceramics

I. Dental Composite, Resin, Sealant, and Cement Chemistry and Development

A. New Monomers for Reducing Polymerization Shrinkage

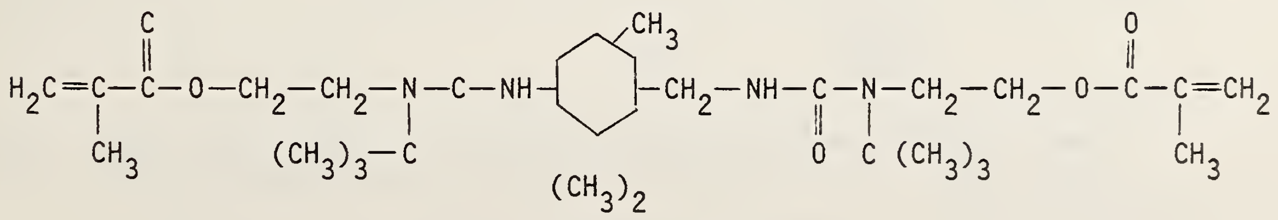
1. Diurea Dimethacrylate Monomer

The synthesis of the diurea dimethacrylate, DTBAEM-HDI, from the reaction of N-t-butyl-2-aminoethyl methacrylate (TBAEM) and hexamethylene diisocyanate (HDI) was described in a previous report [1]. This very bulky white, waxy solid monomer has a molecular weight of 538 vs 512 for BIS-GMA. It has two tri-substituted urea groups, each with a bulky t-butyl substituent.

Employing diluent monomers commonly used with BIS-GMA, formulations giving adequate setting times and yielding composites with very good color stability and diametral tensile strengths well above the ADA specification minimum (34 MPa) were produced (Table 1).

Water sorption measurements of comparable formulations (5A, 5B of Table 1) indicated that the DTBAEM-HDI composite sorbed 0.77 ± 0.01 mg/cm^2 vs 0.55 ± 0.01 mg/cm^2 for the BIS-GMA composite. The water sorption could likely be lowered by increasing the fraction of DMGDMA employed or by incorporating a more hydrophobic diluent monomer.

A second diurea dimethacrylate with a MW of 592 was synthesized from TBAEM and the alicyclic diisocyanate, isophorone diisocyanate (IPDI). This extremely bulky monomer



DTBAEM-IPDI

TABLE 1

Setting times and 24 hour diametral tensile strengths of experimental composites* based on DTBAEM-HDI

Formulation	Monomer System	Wt.%	Setting Time (min.)	Diametral Tensile Strength ± Std. Dev. in MPa (No. of Specimens)
1	TBAEM-HDI	77.0	3.0	43.7 ± 2.5 (5)
	NPGDMA	22.7		
	DHPPT[a]			
2	TBAEM-HDI	77.0	2.5	42.6 ± 3.1 (4)
	NPGDMA[b]	22.6		
	DHPPT	0.37		
3**	TBAEM-HDI	75.0	2.0	39.6 ± 3.0 (5)
	HMGDMA[c]	24.7		
	DHPPT	0.3		
4	TBAEM-HDI	75.0	2.0	44.6 ± 3.9 (4)
	HMGDMA	24.7		
	DHPPT	0.3		
5A	TBAEM-HDI	85.0	3.5	45.2 ± 3.5 (5)
	DMGDMA[d]	14.7		
	DHPPT	0.3		
5B	BIS-GMA	85.0	2.0	44.9 ± 2.9 (6)
	DMGDMA	14.7		
	DHPPT	0.3		
6	TBAEM-HDI	82.0	3.5	37.6 ± 2.2 (5)
	TEGDMA	17.9		
	DMSX[e]	0.13		
7***	Same as above			
8	TBAEM-HDI	70.0	1.5	44.8 ± 1.4 (5)
	TEGDMA[f]	29.8		
	DMSX	0.23		
9	TBAEM-HDI	80.0	2.2	42.2 ± 3.4 (5)
	TEGDMA	19.7		
	DHPPT	0.3		
10	TBAEM-HDI	80.0	1.5	46.4 ± 1.5 (5)
	TEGDMA	19.6		
	DHPPT	0.4		

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* Powder/liquid formulations used with P/L = 3 except where noted. Powder is usual glass filler silanized and coated with 1% benzoyl peroxide (BP).

** P/L = 2.5

*** P/L = 2.5 and blended glass filler used (equal parts 1% BP and 0.3% M glass)

[a] DHPPT = N,N-di-(2-hydroxypropyl)-p-toluidine
[b] NPGDMA = Neopentylglycol dimethacrylate
[c] HMGDMA = Hexamethyleneglycol dimethacrylate
[d] DMGDMA = Decamethyleneglycol dimethacrylate
[e] DMSX = N,N-dimethyl-sym-xylidine
[f] TEGDMA = Triethyleneglycol dimethacrylate

is a viscous liquid (rather than a solid as DTAEM-HDI) and should, therefore, yield stable resin formulations with more types of diluent monomers. On mixing DTBAEM-IPDI with triethylene glycol dimethacrylate to give a 4:1 solution, we observed no evidence of phase separation over a period of several weeks. Using 0.2% N,N-dimethyl-3,5-xylidine (DMSX) as the amine accelerator, a powder liquid formulation (P/L = 3) employing silanized glass filler containing 1% benzoyl peroxide evidenced a setting time of three minutes and resulted in a composite with a very white appearance. The diametral tensile and compressive strengths were only marginal, however, e.g., 34 to 204 MPa, respectively.

2. Bulky Monofunctional Diluent Monomers

The quantity of unreacted vinyl groups or, conversely, the degree of polymerization of a hardened dental resin, is influenced by the nature and amount of the diluent monomer employed [2]. While the highest degree of polymerization was reported [3] for the monofunctional monomer diluent methyl methacrylate (MMA), its use as a major diluent monomer leads to increased polymerization shrinkage and poor marginal adaptation.

For MMA we have substituted bulky monofunctional methacrylates. Previously we described the synthesis of a monofunctional tricyclic aliphatic methacrylate, MAC (MW = 292). Table 2 demonstrates use of this unique monomer in several formulations where it comprises all or a major portion of the diluent monomer.

Table 2

Setting Time and Diametral Tensile Strength of an Experimental Composite* Employing MAC as the Primary Diluent

Experimental		Formulations	P/L	Setting Time (min.)	Diametral Tensile Strength
A	BIS-GMA	64.8%	3	3.0	45.2 ± 1.4 (4)
	MAC	26.4%			
	CDMDMA[a]	8.6%			
	DMAPE[b]	0.2%			
B	BIS-GMA	71.0%	2	2.5	40.8 ± 2.1 (4)
	MAC	28.8%			
	DMAPE	0.2%			

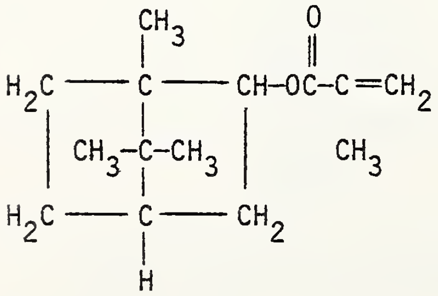
[a] Cyclohexane dimethanol dimethacrylate

[b] 4-N,N-dimethylaminophenethanol

*Powder is same as used in table 1

As can be seen from these results, both the curing characteristics and mechanical properties are in the acceptable range for a dental composite material. The initial color and color stability of these composites were excellent.

A less bulky alicyclic methacrylate is also undergoing evaluation as diluent monomer.



Isobornyl methacrylate (IBM)

As can be seen by the results summarized in Table 3, the use of IBM as a diluent monomer gave composites having acceptable setting times and diametral tensile strengths. Both the initial color and the color stability of these composites were excellent.

Table 3

Setting time and diametral tensile strength of experimental composites employing IBM as the diluent monomer

Formulation	Monomer System, Wt. %		P/L	Setting Time (min).	Diametral Tensile Strength ± Std. Dev. in MPa (No. of Specimens)
1	BIS-GMA	79.8	3	2.0	46.9 ± 2.3 (4)
	IBM	19.9			
	DHPPT	0.3			
2	BIS-GMA	69.8	3	2.5	44.9 ± 2.4 (6)
	IBM	29.9			
	DHPPT	0.3			
3	DTBAEM-HDI	85.0	3	3.0	42.2 ± 0.9 (5)
	IBM	14.7			
	DHPPT	0.3			

3. Hydrophobic BIS-GMA Type Monomers

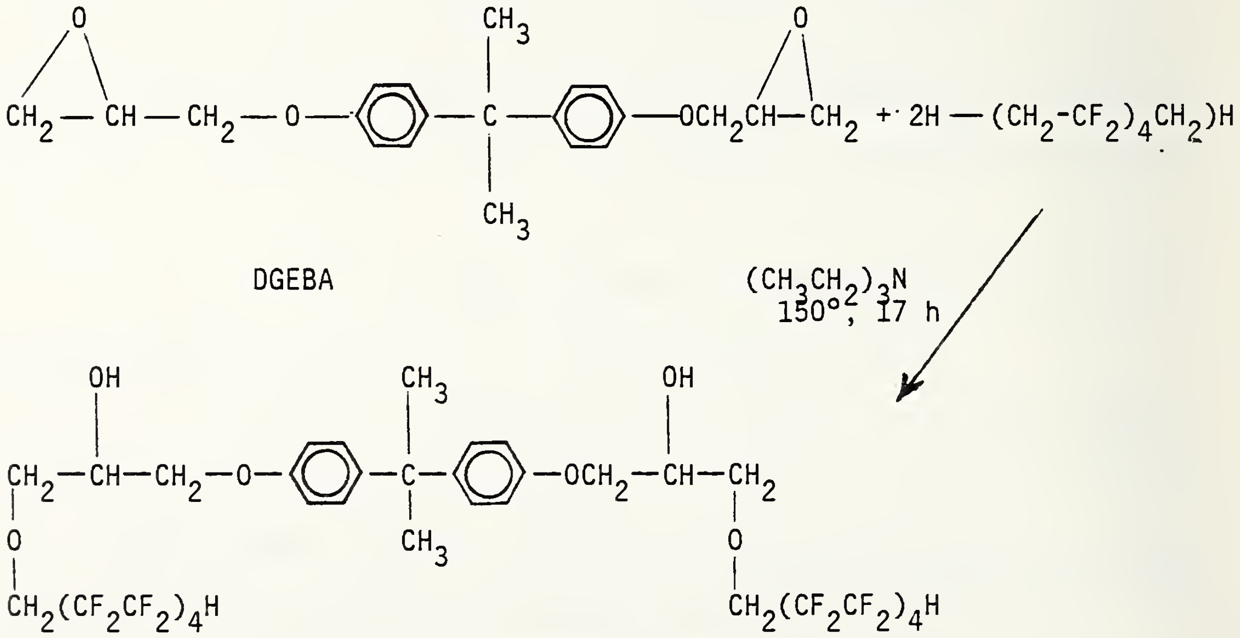
Previous studies [4-6] on the use of highly fluorinated dental monomer systems for enhancing the hydrophobicity of composite and sealant materials indicated the need for thermosetting or crosslinking fluorinated monomers for achieving adequate mechanical strength. Unfortunately, at present only highly fluorinated monomethacrylates and one fluorinated precursor of a dimethacrylate, the very expensive hexafluoropentane-1,5-diol, are currently commercially available.

The least expensive of the commercially available, highly fluorinated alcohols are those based on the telomerization of tetrafluoroethylene with methanol. These telomer alcohols are much more acidic than their hydrocarbon analogs having dissociation constants almost four powers of ten higher than, for example, ethanol. Their general structure is shown below

$$H\text{-}(\text{-}CF_2\text{-}CF_2\text{-})\text{-}_nCH_2OH$$

where n = 1.5.

We have explored the reaction of the higher members of this series, i.e., n = 3.5, with diepoxy compounds such as the diglycidyl ether of bisphenol A (DGEBA) as a means of synthesizing highly fluorinated, bulky diols which may then be converted by standard chemical procedures to the corresponding diacrylate or dimethacrylate monomers. The first member of this series of diols was prepared from DGEBA and $H\text{-}(CH_2\text{-}CF_2)_4CH_2OH$ by heating two parts of the fluorinated alcohol with one part of diepoxy compound at 150° for 17 hours in the presence of one percent triethylamine as the catalyst.



MW = 1204

After isolation, the product was a pale yellow highly viscous liquid. While IR analysis supported the assigned structure we now postulate that the product is probably a mixture of oligomers of various molecular weights. Solubility studies using n-heptane and methylene chloride resulted in three fractions.

Fraction I (about 10 percent of the product) was soluble in n-heptane. Fraction II (about 45 percent) was reasily soluble in methylene chloride. Fraction III (about 45 percent), a very viscous material, was soluble in methylene chloride after several hours at room temperature. IR analysis failed to reveal significant chemical structural differences among the three fractions. The disappearance of the epoxy absorption band of DGEBA and the appearance of a strong OH band was a positive indication that the reaction had occurred.

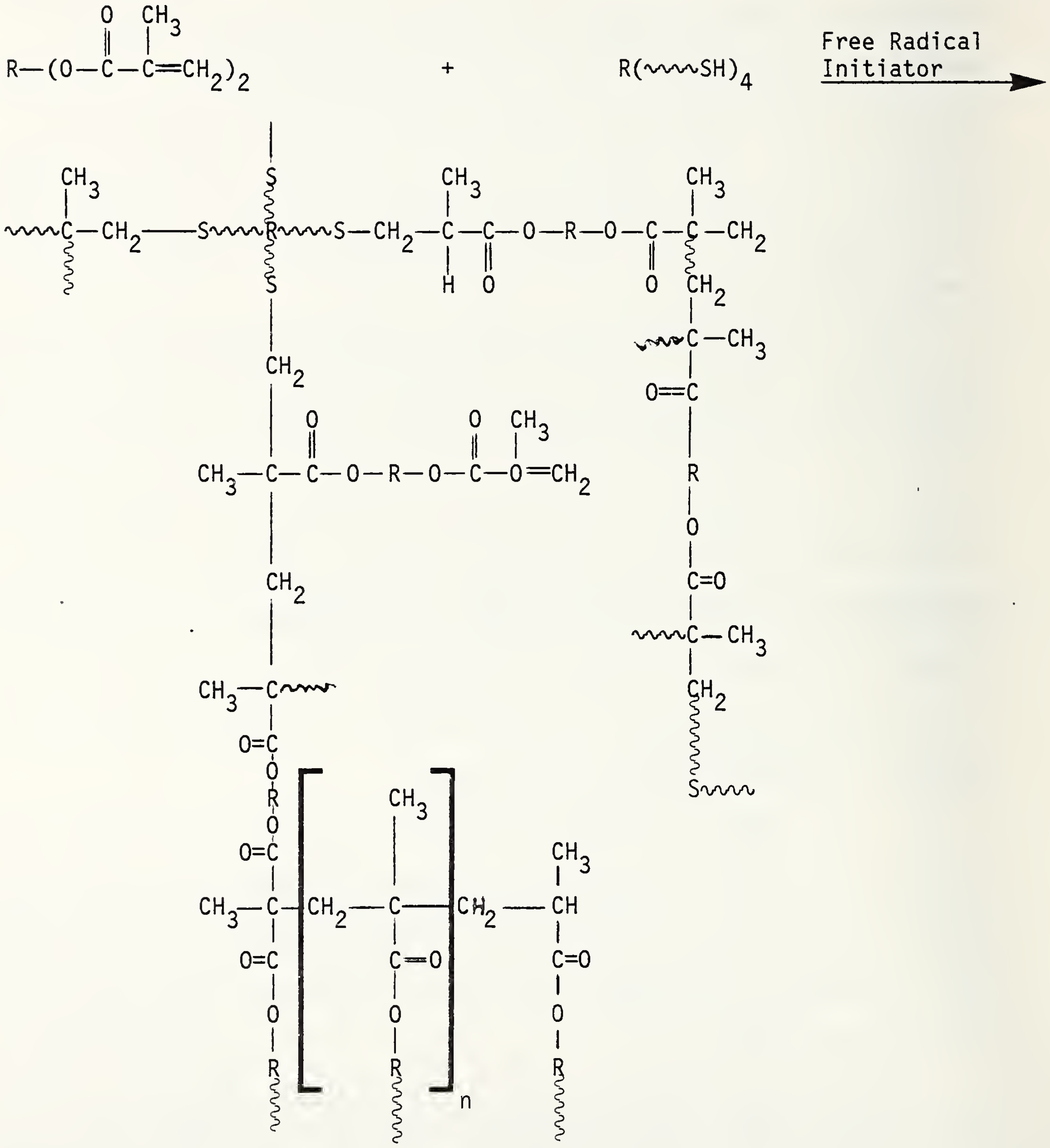
Part of the original unfractionated product was dissolved in methylene chloride and allowed to react with methacryoyl chloride using triethyl amine as the hydrogen chloride accepter. After the usual isolation procedure a yellow, highly viscous oil was obtained. IR analysis did reveal the presence of both ester and vinyl structural features, but some OH units remained unchanged. The product could be polymerized by conventional ambient free radical techniques, but the polymerization was rather sluggish. Purification of the fluorinated polyol is probably needed to obtain a purer monomer which should give faster and more complete cures.

4. Non-Vinyl Agents (Polythiol) Reactive Types

Another approach that holds promise not only toward reducing residual vinyl unsaturation but also of reducing polymerization shrinkage and of enhancing the oxidative stability of the polymer matrix is the use of bulky polythiols.

The free radical addition reaction of monothiols (RSH_2SH) to olefins, the well-known chain transfer reaction, is a classical method of regulating the molecular weight of vinyl polymers. With multifunctional thiols, i.e., $R(CH_2SH)_\chi$ where $\chi \geqq 2$, and polyenes, i.e., $R(CH{=}CH_2)_y$, where $y \geqq 2$, chain extension and crosslinking occur to give vinyl polymers having polythioether elements in their structure [7].

A simplified representation of this type of thiol/ene polymerization is illustrated below.


$$R-(O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2)_2 + R(\sim SH)_4 \xrightarrow{\text{Free Radical Initiator}}$$

Adding relatively small amounts of the polythiol, pentaerythritol 3-mercapto propionate-(PETMP), to a BIS-GMA monomer system gave a resin system that was less subject to air inhibition than conventional dental methacrylate resins. In addition, it was observed in curing by the usual benzoyl peroxide-amine accelerator type initiator system that composite and sealant materials set faster with the addition of the polythiol. In order to obtain a workable setting time, the amount of amine accelerator that was customarily used had to be reduced drastically. The cured composite specimens possessed excellent esthetics because of the reduced amine concentration and the presence of the polythiol elements and enhanced color stability. Depending on the concentration of PETMP both the setting time and the tensile strength could be varied. With high concentrations of PETMP ($<$ 20 percent) composites with relatively low diametral tensile strength (23 to 34 MPa) were obtained due to the increased flexibility of the polymeric matrix. With lower concentrations of PETMP (e.g., 1 to 5 percent) composites of a harder nature were obtained (DTS 34 to 52 MPa).

With the non-amine initiator system, benzoyl peroxide/ascorbyl palmitate, PETMP in concentrations up to 14 percent did not significantly reduce the setting time of the composite material. However, PETMP does appear to improve the storage stability of monomer solutions containing ascorbyl palmitate. After six weeks the same setting time of 4-1/2 minutes was obtained for a formulation of 64.4 percent BIS-GMA, 27.6 percent DMGDMA (decamethylene glycol dimethacrylate), 7.3 percent PETMP, and 0.66 percent ascorbyl palmitate when cured with silinized glass coated with one percent benzoyl peroxide (powder/liquid ratio = 3).

Several typical formulations with PETMP are shown below in table 4.

Table 4

Setting time and 24-hour diametral tensile strength (DTS) of experimental composites formulated with PETMP

Formulation	Composition	Setting Time (min.)	DTS + STD. DEV. (MPa) No. of Spec.
A	BIS-GMA (54%) DMGDMA (20%) PETMP (26%) DHPPT (0.24%) BHT (0.16%)	Too fast to measure	
B	BIS-GMS (68.4%) TEGDMA (29.3%) PETMP (2.2%) DHPPT (0.11%)	1.5	52.2 ± 4 (5)
C	BIS-GMA (68.8%) TEGDMA (29.5%) PETMP (1.1%) DHPPT (0.056%)	2.5	48.8 ± 1.7 (5)
D	BIS-GMA (67.1%) TEGDMA (28.9%) PETMP (3.5%) AP (0.64%)	4.5	41.7 ± 2.2 (5)
E	BIS-GMA (53.3%) DMGDMA (27.6%) PETMP (7.3%) AP (0.66%)	4.5	3.3 ± 1.3 (5)

Polythiols such as PETMP have been shown to be effective reducing agents for UV photosensitizers such as benzophenone [7]. We have also shown that they can be used in visible light photocuring systems that employ diketones such as camphorquinone. With the following resin formulation of 80.2 percent BIS-GMA, 14.2 percent DMGDMA, 5.4 percent PETMP, and 0.2 percent camphorquinone a visible light source (Caulk) gave cures in 20 seconds to a depth of 2 mm in composites formulated with 75 percent by weight of silanized glass. Samples of this same composite when cured for one minute gave specimens of excellent esthetics and color stability with DTS values of 43.5 ± 1.3 MPa. Again the curing of these specimens in air showed less air sensitivity than those cured without PETMP.

5. Expanding Monomer Types

Effort in this fiscal year has been restricted to developing a cooperative education (graduate degree) program wth Maryland University Chemistry Department. Mr. Jeff Stansbury has begun this program with Dr. William Bailey who has been a pioneer in the area of expanding monomer types [8]. We anticipate the work will emphasize monomers that are compatible with methacrylate diluents and have appropriate solubility parameters.

B. Development of Improved Initiator/Accelerator Systems

1. Initiator Research

The results of our investigation into more stable peroxyesters and hydroperoxides as initiators for the polymerization of dental resins were summarized in the preceding annual report [4] and were presented at the IADR/AADR meeting in Chicago.

We have begun examination of new photochemical polymerization initiating systems that could be predicted to be biocompatible on the basis of structure. Several tertiary aromatic amines which we have established to have widely different reactivity toward benzoyl peroxide have been looked at for their capacity to accelerate resin polymerization initiated by camphorquinone. Little difference in rates of cure was noted whether accelerators known to be fast acting with benzoyl peroxide, e.g., 4-N,N-dimethylaminophenylacetic acid or slow acting such as 4-N,N-dimethylaminobenzoic acid, were exposed to a quartz line projection lamp (19 V, 80 W), employed in a fiber optic light.

One especially reactive composite formulation consisted of BIS-GMA (7)/ TEGDMA (3) and 70 percent by weight of silanized glass filler combined with a photoinitiator system of 0.2 percent 4-EDMAB* and 0.1 percent camphorquinone. This formulation cured to a depth of 9 to 10 mm with a three minute exposure to the light source.

We have found that the combination of riboflavin (0.01 percent) (Vitamin B_2) and ascorbic acid (0.7 percent) (Vitamin C) in an aqueous ethanol system is capable o polymerizing methyl methacrylate in a few hours. A problem to be dealt with is that riboflavin has only modest solubility in water and is virtually insoluble in the usual dental monomer systems. However, a yellow paste BIS-GMA based composite formulation with a minute quantity of riboflavin and 0.7 percent ascorbyl palmitate (AP) cured to a white product in two minutes between glass slides when exposed to sunlight. After three minutes of sunlight exposure the same formulation when placed in a Teflon mold and covered with glass slides, cured to a depth of 3 mm. We intend to prepare an organophilic derivative of riboflavin and to examine this approach to photoinitiation further.

2. Amine Accelerators

a. Development of Fast-Acting Biocompatible Amine Accelerators

The development of fast-acting amine accelerators that impart maximum color stability to composites and should be much more biocompatible than the presently used amine accelerators was completed. Three amines, p-(dimethylamino)phenethanol, p-(diethylamino)phenyl acetic acid and its ethyl ester, shown previously to be most promising as accelerators for dental composites, have been synthesized in larger quantities and offered to cooperating laboratories to determine toxicological and biocompatibility characteristics. The accelerator, p-(dimethylamino)phenethanol, synthesized and evaluated pre-

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*Ethyl, 4-N,N-dimethylaminobenzoate

viously in this laboratory has now been made available in research quantities by a chemical manufacturer.

Synthesis of high-molecular weight ester derivatives of p-(dialkylamino)-phenethanol containing free carboxylic acid groups were attempted since these types of organic structure appear to provide great accelerative reactivity for the curing of composites.

After several unsuccessful attempts mono-p-(diethylamino)phenethanol succinate was prepared from 5 g (0.026 mol) of p-(diethylamino)phenethanol and 7.81 g (0.078 mol) succinic anhydride in 25 ml acetone. After evaporation of solvent and purification a thick amber-colored oil ($n_d^{20.5}$ = 1.5230) remained. This compound had an infrared spectrum consistent wth its chemical structure, and a purity of 94 to 95 percent as determined from gas chromatographic analysis at 160 °C. It appears to decompose at higher temperature.

Similarly, the mono-p-(diethylamino)phenethanolmaleate was synthesized since it was expected that this compound would be an excellent accelerator that might have the added advantage of copolymerizing in the curing of the composite. A viscous dark brown oil (n_d^{22} = 1.5416) was obtained. The oil was an effective accelerator for the curing of composites, but the purification of the compound was difficult. The mono-p-(diethylamino)-phenethanol methacrylate was obtained from p-(diethylamino)phenethanol and methacryl chloride in the presence of triethylamine. The compound distilled at 160 to 165 °C/4 mm, n_d^{22} = 1.5380, but had a deep dark-red coloration which made it unsuitable as an accelerator for dental composites.

The mono-p-(diethylamino)phenethanol succinate was incorporated as accelerator into typical powder-liquid composite formulations. The bulk of material hardened, but a soft layer remained at the surface, probably caused by air inhibition. The cause for this air inhibition is unknown.

Two papers [9,10] resulting from these investigations were published in 1981.

b. Amine Accelerators with Intermediate Accelerative Reactivity

As a means to correlating amine structures with their accelerative reactivity, when used with benzoyl peroxide as the initiator, we have investigated slow, moderate, and fast acting amines.

Representatives of these moderately reactive accelerators are N,N-bis(2-hydroxyethyl)-p-toluidine (DHEPT), which is widely used in chemically activated dental restorative resins, and N,N-bis(2-hydroxypropyl)-p-toluidine (DHPPT). Although both amines are solids, DHPPT is more easily purified than DHEPT since it has a higher melting point, 109 to 110 °C. We produced a highly purfied sample of DHPPT and are using this white, crystalline solid amine to study the effect of concentration on the setting time and diametral tensile strength of dental composite materials. In table 5 are summarized the results obtained for powder/liquid formulations based on BIS-GMA (7)/TEGBMA (3) as the resin component. Even at extremely low concentrations (e.g., 1.1 mmol/kg) composite specimens having adequate setting time and diametral tensile strengths (DTS) were obtainable. The initial color and color stability of these composites were excellent. As expected, as the amine concentration increased, both the initial color and the color stability of composites were adversely affected. For concentrations higher than 12.6 mmol/kg, it was necessary to add BHT to obtain workable setting characteristics. A significant decrease in DTS (about 15 percent) was noticed for the 12.7 mmol/kg formulation when 0.09 percent BHT was added.

Table 5

Effect of DHPPT concentration on the setting time and 24-hour diametral tensile strength of an experimental composite[*] formulated with BIS-GMA (7)/TEGDMA (3)

DHPPT Concentration		Setting Time (min.)	Diametral Tensile Strength ± Std. Dev. in MPa (No. of Specimens)
Wt.%	mol^{-3}/kg		
0.42[a]	18.8	3.4	52.0 ± 2.7 (5)
0.32[a]	14.4	4.0	51.3 ± 1.8 (5)
0.28[a]	12.6	5.5	51.0 ± 2.2 (4)
0.28	12.6	1.5	58.4 ± 2.4 (5)
0.16	7.2	2.0	51.8 ± 2.4 (4)
0.10	4.5	2.5	50.4 ± 1.6 (5)
0.05	2.2	3.0	47.7 ± 1.3 (4)
0.025	1.1	5.0	42.3 ± 1.0 (5)

[*] Corning Glass 7724 (325 mesh) silanized with 3-methacryloxypropyltrimethoxysilane and coated with one percent benzoyl perozide. A powder/liquid ratio (P/L) of 3 was used.

[a] In these formulations, 0.09 percent of 2,6-t-butyl-p-cresol (BHT) was added to the liquid components.

A similar study was performed using a commercial diurethane dimethacrylate resin system in place of the BIS-GMA resin system. The results shown in Table 6 paralleled those observed in Table 5 showing the dependence of setting time and DTS on the concentration of DHPPT. The initial color and color stability of these composites was somewhat better than those based on BIS-GMA for the same DHPPT concentration.

Excellent results also were obtained from a paste/paste system that was formulated using BIS-GMA (7)/TEGDMA (3) as the resin and DHPPT as the accelerator. The catalyst paste (P/L = 3) contained one percent BP stabilized with 0.7 percent tyrosine and the accelerator paste (P/L = 3) contained 0.4 percent DHPPT and no added stabilizer. Equal parts of the two pastes

Table 6

Effect of DHPPT concentration on the setting time and 24-hour diametral tensile strength of an experimental composite* formulated with a diurethane dimethacrylate resin**

DHPPT Concentration Wt. %	mmol/kg	Setting Time (min.)	Diametral Tensile Strength ± Std. Dev. in MPa (No. of Specimens)
0.25	11.2	1.5	57.6 ± 4.7 (4)
0.16	7.2	2.0	56.9 ± 3.2 (5)
0.10	4.5	2.5	47.5 ± 3.7 (5)
0.05	2.2	3.5	49.8 ± 1.1 (5)
0.025	1.1	5.0	40.4 ± 3.2 (5)

*Same powder and powder/liquid ratio as used in Table 4.
**From Vivadent

gave composite specimens setting in four minutes and having a DTS of 50.2 ± 3.1 MPa.

As a moderately reactive amine accelerator of high purity, DHPPT is expected to be useful in our work to elucidate the mechanisms of the complex amine-peroxide reactions.

3. Non-Amine Accelerators

We have shown previously that ascorbic acid (AA) or its palmitate ester (AP) functioned best as a polymerization accelerator if used in powder/liquid formulations. That is, the storage stability of the ascorbic acid accelerator is maximized by keeping it in the solid state coated on the glass filler component. This necessitates the dissolution of the peroxide initiator in the monomer system (liquid component), which, especially in the case of benzoyl peroxide, makes it difficult to improve the storage stability of the formulation.

We have been investigating how AP behaves in the dissolved state by studying the effect of various concentrations of dissolved AP on the properties of a normal powder/liquid dental composite material. A series of solutions of AP in BIS-GMA (7)/TEGDMA (3) were prepared and used with a typical silanized glass powder coated either with one percent benzoyl peroxide (Table 7) or one percent t-butyperoxymaleic acid (Table 8). The variation of setting times and DTS with AP concentration for composites prepared with one percent BP powder are shown in Table 7. For freshly prepared solutions there seems to be little variation in setting times on increasing the concentration of AP almost tenfold(0.1 mmol/kg to 0.9 mmol/kg). This is in contrast to the behavior observed with amine accelerators. The effect of AP concentration on DTS more nearly parallels the results found with amine accelerators.

Table 7

Effects of ascorbyl palmitate concentration on setting time and diametral tensile strength of an experimental composite material* using benzoyl peroxide as an initiator

Ascorbyl Palmitate Concentration Wt. %	mmol/kg	Setting Time (min.)	Diametral Tensile Strength MPa = Std. Dev. (No. of Specimens)
0.1	2.4	4.0	35.1 ± 1.6 (6)
0.2	4.8	3.0	37.4 ± 1.3 (6)
0.3	7.3	4.0	37.8 ± 2.3 (6)
0.4	9.7	3.5	41.1 ± 1.6 (6)
0.5	12.1	3.75	41.1 ± 2.5 (5)
0.6	14.5	4.0	42.7 ± 2.0 (6)
0.7	16.9	3.75	44.1 ± 1.6 (5)
0.8	19.3	4.25	45.8 ± 1.4 (6)
0.9	21.8	4.0	43.9 ± 2.2 (6)

*Powder/liquid formulations employing powder/liquid ratio of 3. Powder is a silanized glass filler and coated with one percent BP. Liquids are monomer mixtures consisting of seven parts BIS-GMA and three parts TEGDMA containing the indicated concentrations of ascorbyl palmitate. No BHT was added.

Table 8

Effects of ascorbyl palmitate concentration on setting time and diametral strength of an experimental composite material* using TBPM as an initiator

Ascorbyl Palmitate Concentration Wt. %	mmol/kg	Setting Time (min.)	Diametral Tensile Strength MPa = Std. Dev. (No. of Specimens)
0.1	2.4	6.25	35.1 ± 3.3 (6)
0.2	4.8	5.5	36.6 ± 2.9 (4)
0.3	7.3	4.25	47.2 ± 2.0 (7)
0.4	9.7	6.5	45.0 ± 1.8 (8)
0.5	12.1	4.0	47.9 ± 1.4 (4)
0.6	14.5	6.0	44.4 ± 2.2 (6)
0.7	16.9	4.25	48.3 ± 1.0 (5)
0.8	19.3	4.25	46.5 ± 1.7 (6)
0.9	21.8	4.25	45.2 ± 3.5 (4)

*Same as Table 6 except one percent TBPM was used as an initiator instead of one percent BP.
TBPM = t-butylperoxymaleic acid

The effect of AP concentration on DTS more nearly parallels the results found with amine accelerators.

With composites prepared using the one percent TBPM powder (Table 8), a greater but somewhat erratic variation of setting time with the concentration of AP was observed. The setting times, in some cases, are somewhat longer for TBPM than for BP formulations. However, on the average, DTS values tend to be somewhat higher for the TBPM formulations.

The initial color of both types of composites was excellent. The color stability of the AP/TBPM composites was superior to those prepared with the AP/BP initiator system, although the latter were excellent compared to that of the usual amine/BP composites.

All the AP solutions in BIS-GMA (7)/TEGDMA (3) showed loss of accelerative efficacy on storage in the dark in glass vials at 22 °C after 30 days. However, the more concentrated solutions (e.g., 0.6 to 0.9 percent) still gave acceptable setting times (7 to 8 minutes vs the original 3 to 4 minutes) when measured using one percent BP powder (P/L = 3) at 37 °C.

Several potential stabilizing agents have been added to new AP solutions. The most promising stabilizers used thus far appear to be the combination of sodium bisulfite ($NaHSO_3$) and dihydroxymaleic acid. A solution of 0.7 percent AP in BIS-GMA (7)/TEGDMA (3) containing 0.04 percent dihydroxymaleic acid and 0.07 percent $NaHSO_3$ has retained its original setting time of 4.0 minutes after three months using one percent BP powder.

4. Vacuum Polymerization of Composite Resins

A recent article reports that the use of a relatively short application of vacuum during the preparation of a dental composite had several beneficial effects on the finished composite [11]. A significant reduction in the porosity and surface roughness was noted. The reduced porosity apparently increased the diametral tensile strength by about 11 percent. Since the removal of oxygen supply by vacuum application shortened the initiation of polymerization time drastically, it was necessary to add a retarder to the composite mix in order to obtain workable consistencies.

We have tried a variant of this technique with composite materials based on the AP/BP initiator system which, because of relatively long setting characteristics should not require the presence of a retarder. Our initial experiments indicate that the vacuum technique is quite feasible with ascorbic acid type composite materials and a material of workable consistency is obtained after exposure to house vacuum for 30 to 60 seconds.

The diametral tensile strengths of these composites were ten percent higher than similar composites prepared without exposure to vacuum. This technique needs to be examined with other relatively slow, chemically activated and light cured dental resin composite materials.

C. Analysis for Extent of Polymerization of Dental Resin

The final properties of a dental sealant or composite restorative material are directly related both to the chemical composition of the dental monomer system and to the degree of conversion that has occurred in this monomeric component. It would be helpful in the development of improved dental resin materials to be able to assess rapidly and conveniently the extent of polymerization (EP) of any dental monomer system that can be hardened under control conditions that are clinically relevant.

Several workers have used infrared (IR) spectroscopy to measure the EP of several commercial sealant and composite materials [2,12-14]. These IR techniques measure EP by monitoring the decrease in the carbon-carbon double bond ($>C=C<$) absorbance (1639 cm^{-1}) of the methacrylate monomer(s) that occurs concomitantly with vinyl addition polymerization. In the case of dental composite materials, especially, the traditional IR analytical methods are often hampered by difficulties in sample preparation and by a strong interference in the critical vinyl absorption region by the siliceous filler component. In addition, there may be similar problems of interfering absorption bands with certain monomer systems.

These difficulties may be circumvented to some extent by means of an alternate technique based on differential scanning calorimetry (DSC). Unlike the traditional calorimetric methods, DSC experiments are far less arduous and time consuming and require only milligram quantities of material. Other workers have successfully utilized DSC to study the polymerization of both monofunctional and multifunctional vinyl monomers [15-17].

The monomers used in the present study, their abbreviations, and commercial sources, are given in Table 9. A similar listing of the accelerators used to formulate the various initiator systems with benzoyl peroxide (BP) is given in Table 9a. The materials were used as received. For the composite studies, the filled component was prepared from a barium oxide containing silica glass (No. 7724, 325 mesh) obtained from Corning Glass Works (Corning, NY). The glass powder was silanized with 3-methacryloxypropyltrimethoxysilane (A-174, Union Carbide Corp., New York, NY), by a previously described procedure [18] to give a reinforcing filler with 0.5 percent silane content. A portion of this silanized glass was coated with one percent by weight BP as previously described [19].

Samples were placed in DSC aluminum pans which were hermetically sealed and quickly transferred to the sample holder of a Perkin-Elmer DSC-2. Pans plus seals were weighed prior to the addition of samples. A similar weighed, sealed, but empty DSC pan was used in the reference holder. All polymerization experiments were conducted under nitrogen in either the temperature-scanning or the isothermal mode [20].

The instrument was calibrated using indium, $\Delta H_{(fusion)} = 680$ cal g^{-1}, MP 156.4 °C. For the thermally initiated polymerizations of specimens containing only BP as the initiator the usual sampling technique of obtaining an initial (unpolymerized) and a final (polymerized) weight for the specimen was used (Tables 11 and 12). The comparison of the two weighings indicated that essentially no material loss occurred during the scan.

With two component formulations (Tables 13-16), the peroxide and accelerator portions were weighed onto separate sections of a small aluminum dish. The separated components were then combined and mixed thoroughly for one minute before transfer of an aliquot to a DSC pan which was then sealed.

Table 9

Monomers Used in DSC Study

Name	Abbreviation	Source
2,2-BIS[p-(γ-methacryloxy-β-hydroxypropoxy) phenyl]propane	BIS-GMA	Freeman Chemical Co. (Milwaukee, WI)
Triethylene glycol dimethacrylate	TEGDMA	Esschem Co. (Essington, PA)
2,2-BIS[p-(β-methacryloxyethoxy)phenyl]propane	BIS-EDMA	Espe GmbH (Seefeld, Germany)
Isobornyl methacrylate	IBM	Polysciences (Warrington, PA)

Table 9a

Accelerators Used in DSC Study

Name	Abbreviation	Source
p-tert-Butyl-N-N-dimethylaniline	DMBA	Aldrich Chemical Co. (Milwaukee, WI)
4-Dimethylaminobenzoic acid	4-DMAB	"
Ethyl-4-dimethylaminobenzoate	4-EDMAB	"
N,N-BIS(2-hydroxypropyl)-p-toluidine	DHPPT	Ivoclar, AG (Shaan, Liechtenstein)
Ascorbyl palmitate	AP	Hoffman-LaRoche, Inc. (Nutley, NJ)

Table 10

Molar Heats of Polymerization of Methacrylate Monomers

Monomer	ΔHp kcal/mol	Reference
Methyl methacrylate	13.8	23
Ethyl methacrylate	13.8	23
n-Propyl methacrylate	13.7	23
n-Butyl methacrylate	14.3	23
n-Hexyl methacrylate	14.4	23
Lauryl methacrylate	13.6	17

Table 11

Extent of Polymerization (EP) of Thermally[1] Initiated Polymerizations by DSC

Monomer	BP Concentration	T_p[2] (°C)	ΔH (cal/g) ± Std. Dev. (No. of Specimen)	EP (% >C--C< reacted)
IBM	1.0	115	55.3 ± 1.9 (3)	90.3
BIS-EDMA	1.0	72	28.6 ± 1.0 (3)	47.7
BIS-GMA (7) TEGDMA (3)	1.0	90	34.2 ± 1.2 (3)	52.0
"	0.39	95	28.6 (1)	43.5
"	2.2	90	40.7 (1)	61.9
TEGDMA	1.0	92	82.3 ± 1.5 (3)	86.3
"	2.0	86	81.3 ± 1.2 (3)	85.5

[1] Thermal scan rate = 2.5 deg/min.

[2] T_p = peak temperature of DSC curve.

Table 12

EP of Poly[BIS-GMA(7)/TEGDMA(3)] as a Function of BP Concentration and Thermal Scan Rate

Thermal Scan Rate (deg/min)	0.39			1.0			2.2		
	ΔH cal/g	EP %	T_p °C	ΔH cal/g	EP %	T_p °C	ΔH cal/g	EP %	T_p °C
0.62	25.5	38.8	85	34.8	52.9	86	32.1	48.8	84
1.25	27.6	42.0	90	36.5	55.4	90	39.1	59.4	89
2.5	28.6	43.5	95	35.2	53.4	90	40.7	61.9	90
5.0	32.2	48.9	102	37.3	56.7	102	40.4	61.4	100
10.0	49.1	74.6	110	41.0	62.3	109	42.6	64.8	107
20.0	36.0	54.8	119	40.9	62.2	118	42.1	63.9	115

The sample weight was obtained after the run by subtracting the weight of the pan plus seal from the final weight, assuming no significant loss of material.

The observed heat of polymerization, ΔH_{obs}(cal g^{-1}), is based on the planimeter measurement of the total area under the recorded curve or curves. In several representative DSC experiments, a base line for the thermal scans was obtained by a second thermal scan of the polymerized material over the same temperature range [21,22].

The exothermic heat of reaction (enthalpy) arising from the free radical polymerization of methacrylate monomers is directly proportional to the number of vinyl groups undergoing this self addition reaction, assuming the absence of any significant side reactions. The molar heat of polymerization, ΔHp, is the heat evolved during the complete polymerization of one mole of monomer and is a primary thermodynamic quantity determined only by the initial and final states of the monomer and polymer, respectively, and independent of the mechanism of polymerization. ΔHp's have been determined by various methods for a series of methacrylate monomers. The ΔHp values of several representative monofunctional methacrylates are given in Table 10.

As a basis for calculating the degree of conversion of monomer to polymer or the EP of the dental monomer systems used in this study, the ΔHp value of lauryl methacrylate (LMA), a bulky (molecular weight = 254), monofunctional methacrylate was chosen as a standard. The ΔHp value for LMA, as determined in a similar DSC study, is 13.6 kcal/mol [17]. A basic assumption of this method is that heat of reaction for the conversion of a vinyl group to saturated carbon-carbon bond is the same for all methacrylate monomers and only proportional to the number of reacted vinyl groups. Thus, for 100 percent conversion, the ΔHp of LMA should be the same as that of methyl methacrylate (MMA) or isobornyl methacrylate (IBM) but only one-half that of BIS-GMA or TEDDMA which are difunctional. Conversely, for a monomer mixture of 7 parts BIS-GMA and 3 parts TEGDMA, the ΔHp of this monomer system is twice that of LMA or 2 x 13.6 kcal/mol or 27.2 kcal/mol. For this monomer mixture, the calculated heat of polymerization in calories per gram, assuming 100 percent conversion, is derived as follows:

<u>For 100% Conversion of 1 g of BIS-GMA (7)/TEGDMA (3)</u>

$$\Delta H^{CALC}_{7,3} = (\text{number of moles BIS-GMA} + \text{number of moles TEGDMA}) \times 27{,}200\ \text{cal/mol}$$

$$\Delta H^{CALC}_{7,3} = \left[\frac{0.7}{512} + \frac{0.3}{286}\right] 27{,}200\ \text{cal};$$ where 512 and 286 are the molecular weights of BIS-GMA and TEGDMA, respectively.

$$\Delta H^{CALC}_{7,3} = (0.00242 \times 27{,}200\ \text{cal}$$

$$= 65.8\ \text{cal}$$

Therefore,

$$EP = \frac{\Delta H_{obs}}{\Delta H^{calc}_{7,3}} \times 100;$$ where ΔH_{obs} is the observed heat of polymerization for a BIS-GMA (7)/TEGDMA (3) specimen

Thus, if ΔH_{obs} = 33.0 cal/g,

EP = 33.0/65.8 x 100 = 50.2 percent

Thermally initiated polymerizations using BP as the initiator were conducted by DSC for IBM, a bulky, monofunctional methacrylate, BIS-EDMA, a solid, crystalline dimethacrylate (mp = 44° by DSC), the monomer mixture, BIS-GMA (7)/TEGDMA (3) and TEDGMA alone at the same thermal scan rate of 2.5 degrees per minute. The observed heats of polymerization (ΔH) and the calculated extents of polymerization (EP) for these monomers are given in Table 11. In the case of the solid monomer, BIS-EDMA, the solid initiator, BP, was mechanically dispersed into the monomer first by gentle spatulation using a plastic spatula, and then by gentle shaking in a plastic vial. Samples from this mix were used in the DSC runs. The liquid monomers containing dissolved BP also contained 0.1 percent dissolved BHT (2,6-di-tert-butyl-4-methlphenol) as a stabilizer. For the polymerization experiments employing 1 percent and 2 percent BP, the ΔH values are averages obtained from three runs using specimens of approximately equal size (e.g., 5 to 7 mg). The other results represent single runs. The results in Table 11 illustrate the much higher conversions possible in the case of a monofunctional bulky monomer (IBM) or a flexible dimethacrylate such as TEDDMA compared to that achieved with a rigid functional methacrylate such as BIS-EDMA. The temperature range for these experiments was the same, 27 to 140 °C. Table 11 also illustrates the increase in EP with increasing concentration of BP for BIS-GMA (7)/TEGDMA (3). The temperature, Tp, was the temperature at the peak of the major exothermic curve of the thermogram.

Table 12 summarized the effect of the thermal scan rate and BP content on the EP of BIS-GMA (7)/TEGDMA (3).

For a given thermal scan rate, Tp and the conversion of monomeric units to polymer (EP) usually increased with an increase in the BP concentration. With an increasing thermal scan rate, Tp increased and the conversion values (EP) also tended toward maximum values. The high conversion (EP = 74.6 percent) recorded for the 0.39 percent BP solution at a thermal scan rate of 10 deg/min appears to be an anomalous result. The EP value (54.8 percent) at a thermal scan rate of 20 deg/min is probably more indicative of the maximum conversion for this formulation.

The results shown in Tables 13-16 are for polymerization of the same monomer system using various types of chemical activators for the free radical decomposition of BP. With fast-acting chemical activators, such as

Table 13

EP by DSC[1] for Poly[BIS-GMA(7)/TEGDMA(3)] Chemically Activated Polymerizations--BP/amine accelerator

L_A[2] Amine Acc. & Conc. (Wt. %)	L_{BP}[3] BP Conc. (Wt. %)	L_A/L_{BP} Ratio	T_p (°C)	ΔH (cal/g)	EP (%)
DMBA	0.39	0.45	49	31.0	47.1
(fast)	↓	0.96	44	32.3	49.1
0.23		1.12	41	36.8	56.0
DHPPT	1.0	0.80	61	35.2	53.5
(mod.)	↓	1.01	61	34.3	52.1
0.32		1.35	64	36.7	55.7
0.42	1.0	0.54	57	37.8	57.4
0.42	2.2	1.30	49	31.4	47.8
4-DMAB	1.0	1.11	58	33.8	51.4
(slow)					
0.50	2.2	0.94	56	32.5	49.4

[1] Thermal scan rate = 2.5 deg/min.

[2] L_A = liquid monomer consisting of BIS-GMA(7)/TEGDMA(3) with indicated concentration of amine accelerator

[3] L_{BP} = same liquid monomer as in L_A but with indicated concentration of BP and 0.1 percent BHT.

Table 14

EP by DSC* for Poly[BIS-GMA(7)/TEGDMA(3)] Chemically Activated Polymerization--BP/4-EDMAB

L_A 4-EDMAB conc. (Wt. %)	L_{BP} BP Conc. (Wt. %)	L_A/L_{BP} Ratio	T_p (°C)	ΔH (cal/g)	EP (%)
0.5	1.0	0.84	78	31.2	47.4
1.0	1.0	0.96	66	32.4	49.3
1.3	1.0	0.92	62	34.5	52.4
0.5	2.2	1.04	65	34.6	52.5
1.0	2.2	0.81	57	33.6	51.1
1.3	2.2	0.42	55	33.0	50.2
1.3	2.2	0.52	53	34.0	51.7
1.3	2.2	0.72	52	35.7	54.2
1.3	2.2	1.02	51	31.4	47.7
1.3	2.2	1.72	51	34.4	52.3
1.3	2.2	2.57	52	33.8	50.2

*Thermal scan rate = 2.5 deg/min.

the amine accelerator DMBA, it proved difficult to obtain satisfactory DSC thermograms by normal sampling techniques when BIS-GMA (7)/TEGDMA (3) containing 2.2 or 1 percent BP was used. Special sampling and mixing techniques, such as prior cooling of the two components, may be needed in these cases. However, satisfactory DSC curves were obtained with the 0.39 percent BP solution in BIS-GMA (7)/TEGDMA (3). Moderately reactive amine accelerators (e.g., DHPPT) or those of low reactivity (e.g., 4-DMAB, 4-EDMAB) are better suited to this type of DSC experiment and permit wider ranges of accelerator-initiator concentrations to be explored (see Tables 13 and 14).

It was observed that in polymerizations employing the fast-acting amine accelerator, DMBA, that the Tp's were lower (in some cases unrecordable) than the Tp's obtained with the slower-acting activators. For the chemically-activated polymerizations, the Tp's correlated well with the observed setting times of the formulations. Thus, the formulations that had fast setting times had low Tp's.

The relatively low reactivity of 4-EDMAB toward BP compared to the other amine accelerators permitted a wide activator concentration range to be studied. As shown in Table 14, one significant effect of increasing the concentration of 4-EDMAB relative to BP is to lower Tp to what appears to be a limiting temperature (51 to 52 °C). These results parallel our results on the effect of 4-EDMAB concentration on the setting time of composites [24]. The correlation of 4-EDMAB concentration with EP, however, does not appear to be as straightforward. Both the concentration of the amine and BP as well as the ratio of these two components of the initiator system are important parameters affecting EP [25].

The use of the moderately reactive non-amine accelerator, AP, also is well suited to DSC studies of chemically-activated polymerizations (Table 15).

Table 15

EP by DSC[1] for Poly[BIS-GMA(7)/TEGDMA(3)] Chemically Activated Polymerization--BP/AP

L_A	L_A/L_{BP}[2]	T_p	ΔH	EP
AP Conc. (Wt. %)	Ratio	(°C)	(cal/g)	(%)
0.54	1.10	43	34.6	52.6
0.54	1.40	49	35.0	53.4
0.56	0.80	40	35.2	53.5
0.56	0.94	45	34.4	52.3
0.59	0.91	41	35.9	54.6
0.59	1.33	44	35.1	53.4
0.59	1.59	49	36.4	55.3

[1] Thermal scan rate = 2.5 deg/min.

[2] L_{BP} = BIS-GMA(7)/TEGDMA(3) containing one percent BP and 0.1 percent BHT.

Table 16

EP by DSC* for Poly[BIS-GMA (7)/TEGDMA (3)] Liquid/Liquid Paste/Paste and Powder/Liquid Formulations

Run	Accelerator Part	Peroxide Part	Ratio	T_p (°C)	ΔH (cal/g)	EP %
1 L/L	L_A=0.5% DHPPT In BIS-GMA(7)/TEGDMA(3)	L_{BP}=1.0% BP, 0.1% BHT	1	42	30.5	46.3
2 P/P	Paste: 75%, silanized glass filler +L_A	Paste: 75%, silanized glass filler +L_{BP}	1	45	28.2	42.8
3 Pow/L	Same as in run 1	Silanized glass filler	Pow/L= 2.9	28	29.7	45.2

L = Liquid; P = Paste; Pow = Powder
* Thermal scan rate 2.5 deg/min.

The effect on Tp of increasing the concentration of AP relative to BP by increasing the L_A/L_{BP} ratio does not seem to be the same as that observed for 4-EDMAB, but instead shows an opposite trend. Also, there seems to be less fluctuation in these EP values than was observed with the BP-amine initiator systems. All the EP values for the chemically-activated polymerizations were in the same general range (43 to 57 percent).

The EP values obtained with the chemically-activated polymerizations for a liquid/liquid, a similar paste/paste, and a powder/liquid formulation are compared in Table 16. The somewhat lower EP of the composite from the P/P formulation is probably due to absorption by the glass filler of some of the exothermic heat of polymerization. The low Tp and relatively high EP value for the Pow/L run probably is due to the high BP/amine concentration.

The high EP values observed in the case of the thermal polymerization with BP alone for TEGDMA (see Table 11) were also observed when this monomer is polymerized by chemically activating the decomposition of BP with an amine accelerator. However, on contrast to the single exotherm obtained in the thermal polymerization thermograms, the chemically-activated polymerizations of TEGDMA have thermograms with two distinct exotherms, and therefore, two peak temperatures (T_{p1} and T_{p2}). The results of two different formulations are summarized in Table 17. The effect of doubling the BP and DHPPT concentrations is to lower the peak temperatures without significantly affecting the EP values.

The same type of behavior also was observed on doubling the BP concentration in the thermal polymerization experiment (Table 11).

The organic component of dental composite restorative and sealant materials primarily consists of several methacrylate monomers whose overall functionality is greater than one. The copolymerization of such multifunc-

Table 17

EP by DSC* for Poly(TEGDMA)**
Chemically-activated Polymerizations (BP/DHPPT)

L_A Amine Acc. Conc. (wt.%)	L_{BP} BP conc. (wt.%)	L_A/L_{BP} Ratio	T_{p1} °C	T_{p2} °C	ΔH (cal/g) (± Std.Dev.)	EP
0.50	1.0	1	50	50	79.5 (± 0.9)	83.5
1.0	2.0	1	28	58	78.1 (± 1.0)	82.1

*Thermal scan rate = 2.5 °C/min
**ΔH represents average of three experimental runs for each formulation of L_A/L_{BP}.

tional vinyl monomers, under ambient conditions, leads to the formation of a crosslinked, three-dimensional network polymer having residual unsaturation in the form of pendant vinyl groups and, perhaps, unreacted monomer or oligomeric species as well. Therefore, the properties of this complex network copolymer will be determined not only by the chemical structure and composition of the monomer system, but also by the degree of conversion or extent of polymerization (EP) of the vinyl groups. The presence of unreacted monomer and oligomers can have a plasticizing effect (i.e., lowering the glass transition temperature) on the polymer, thereby altering the physical and mechanical properties of dental materials fabricated from the monomer system. In addition, the presence of pendant residual carbon-carbon unsaturation can make the polymeric matrix more susceptible to oxidative degradative reactions [26,27]. In dental composite materials such chemical degradative reactions, if unchecked by stabilizers, can lead to poor esthetics (i.e., color instability) and poor durability (i.e., loss of anatomic form). It is important, therefore, to be able to assess, at least on a relative basis, the degree of residual unsaturation remaining after the polymerization of various dental monomer systems.

DSC offers a comparatively facile and rapid method for determining the degree of conversion of vinyl monomers to polymer. The EP values of a variety of polymerized dental monomer systems can be compared under the same conditions as a means of selecting those having the least residual unsaturation. Thus, for a given principal monomer (e.g., BIS-GMA), the effect of the diluent monomer's structure and composition can be evaluated. For example, the use of a bulky nonfunctional methacrylate and a smaller quantity of a flexible dimethacrylate may result in a more complete polymerization of a rigid dimetacrylate such as BIS-GMA or BIS-EDMA.

Another potential area of application for DSC is in the evaluation of inhibitors for dental monomers with a view toward improving the storage life of dental materials based on vinyl monomers. It has been shown that DSC can be a rapid, quantitative method for determining the effectiveness of various inhibitors of vinyl polymerization [28].

D. Resin/Filler Coupling Improvement

Previous results showed that addition of n-propylamine to 3-methacryloxypropyltrimethoxysilane (A-174) dissolved in cyclohexane enhanced the silanization of silica. This treatment also yielded a more stable SiO_2-silane bond on storage of the silanized silica in water at elevated temperature (Table 18). On thermocycling in water for one week the high initial tensile strength of the n-propylamine-silanized silica composite dropped 39.7 percent, but leveled off on further thermocycling. The lower tensile strength of composite specimens containing silica not treated with n-propylamine decreased 24.5 percent after one-week cycling but decreased continuously on further exposure to water. The rather low strength properties of the

Table 18

Effect of Thermocycling Time on Resin-Filler Bonding as Judged by Measured Tensile Strength of Composites

	Tensile Strength, MPa			
	0	1 week	2 weeks	3 weeks
Composite* containing fumed silica treated with A174** and tripropylamine in cyclohexane	18.1±1.0	10.9±0.6	9.3±0.7	9.5±0.9
Composite* containing fumed silica treated with A174 in cyclohexane	9.4±0.5	7.1±0.4	6.3±0.5	5.4±0.1

Thermocycling at 5 to 55 °C

*Composition of the composite:

Benzoyl peroxide paste, percent by weight

BIS-GMA	53.62
TEGDMA	22.99
BHT	0.154
Benzoyl peroxide	0.766
Filler	22.47

Amine Paste, percent by weight

BIS-GMA	53.88
TEGDMA	23.11
BHT	0.154
Dimethyl-p-toluidine	0.386
Filler	22.47

**3-methacryloxypropyltrimethoxysilane

composites prepared with the colloidal silica are probably the result of incomplete copolymerization on curing of the methacrylate present on the treated silica and the methacrylate groups present in BIS-GMA and diluent monomer.

Further results of the dependence of the effectiveness of the silanization on the specific amine is shown in Table 19. Aromatic and heterocyclic

Table 19

The Effect of Amines on the Silanization of Silica Surfaces

Amines	Basicity	Bonding, %*
Primary amines		
n-propylamine	3.84×10^{-1}	100
sec-butylamine	--	100
tert-butylamine	4.79×10^{-4}	100
Secondary amines		
diethylamine	9.5×10^{-4}	100
dipropylamine	1.0×10^{-3}	100
di-n-hexylamine	--	100
diisopropylamine	1.09×10^{-3}	72.9
diisobutylamine	1.02×10^{-3}	58.0
Tertiary amines		
triethylamine	5.5×10^{-4}	65.5
tri-n-butylamine	8.52×10^{-5}	68.0
N,N-dimethylbenzylamine	8.14×10^{-6}	52.7
quinuclidine	3.8×10^{-4}	74.8
Aromatic amine		
N,N-dimethylaniline	1.1×10^{-9}	4.7

Fumed silica pellet was treated with A174 and a respective amine (molar ratio = 1 /0.0042 moles) in cyclohexane for 1/2 hour, washed with acetone for ten minutes, and air dried.

*Calculated from relative intensity ratio of IR peaks of 3740 cm^{-1} (free OH bond) and 1850 cm^{-1} (siloxane bond in the silica).

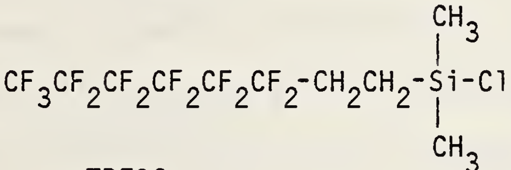
amines are poor catalysts. Primary amines are most efficient probably because of the absence of steric hindrance. On the other hand, diisopropylamine and di-isobutylamine containing bulky side groups attached to the nitrogen atom are much less efficient than diethylamine and di-n-propylamine, two compounds which have about the same basicity constant. For tertiary amines, the efficiency does not appear to be related to the basicity of the amine which may indicate that another reaction mechanism might be involved in the silanization than in the reaction with primary or secondary amines.

Glass particles (Corning 7724) silanized in two different solvents (acetone and cyclohexane) with and without n-propylamine and then stored in water for various lengths of time have been prepared. The treated reinforcing fillers coated with one percent benxoyl peroxide will be incorporated into a composite formulation and the effect of the different silanizing and aging treatments on the physical properties of the cured composites will be determined.

An extension of this work was initiated to investigate the *in vitro* wear performance of experimental composites silanized with and without n-propylamine (see III, this report).

An oral presentation, "Application of Silane Coupling Agent to Inorganic Components of Composites," was presented at the annual meeting of the International Association for Dental Research, Chicago, March 1981.

While improvement in the hydrolytic stability of the coupling between resin and filler has been shown as a result of silanizing the filler in the presence of N-propylamine, it would be desirable to improve this aspect further. One approach in this laboratory and elsewhere has been to explore the use of highly fluorinated dental monomers. A potential problem that may arise from the use of such a highly fluorinated resin matrix with a conventionally silanized glass filler is the possible lack of sufficient compatibility between the two components to give optimum bonding of the polymeric matrix to the glass. To this end, we have initiated a study to explore the efficacy of fluorinated silane coupling agents (i.e., those with polymerizable vinyl groups) commercially available. However, on the possibility that through synergistic interaction we could derive the hydrophobic benefits of a highly fluorinated silane agent that was not a coupling agent if employed with the usual silane coupling agent, A-174, we examined tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane (TDFOS) whose structure is shown below:



$$CF_3CF_2CF_2CF_2CF_2CF_2\text{-}CH_2CH_2\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}\text{-}Cl$$

TDFOS

The silane agent proved very reactive with unsilanized glass filler as evidenced by a mildly exothermic reaction during a silanization procedure using cyclohexane as th carrier solvent.

Initially we applied 0.5 percent of TDFOS to the glass filler by usual silanization techniques but without an amine catalyst (cyclohexane solvent plus 2 hours at 60 °C, followed by rotary evaporation of the solvent and vacuum drying for 24 hours). The second step involved applying 0.5 percent of A-174 to the TDFOS treated glass by the usual procedure (cyclohexane plus 2 percent n-propylamine as the catalyst, etc.). The resulting dual silanized glass was then coated with 1 percent benzoyl peroxide (BP) and used to make composite specimens from a BIS-GMA (7)/TEGDMA (3) resin mixture for diametral tensile strength determination. The DTS values were significantly lower (∿ 30 MPa) than those obtained using the conventional A-174 silanized glass filler coated with 1 percent BP (DTS ∿ 45 MPa). However, by reversing the silanization procedure (i.e., applying A-174 first and TDFOS second) a glass filler was obtained which, when used to prepare composite specimens, gave diametral tensile strengths of better than 40 MPa.

Table 20 summarizes the effect of the dual silanization treatment on the tensile strength of various experimental composite materials. All the specimens were prepared by powder/liquid formulation techniques employing filler coated with 1 percent BP. In addition, the composite specimens containing either of the fluorinated silanized glasses had a much whiter appearance than those prepared with the A-174 silanized glass. Also, they have somewhat better color stability. However, water sorption studies carried out on composites using the new dual silanized glass filler revealed little difference from the water sorption of composites prepared with only A-174 silanized glass.

E. Microporous Glass as Reinforcing Filler for Composites and Denture Base Systems

The objective was to use a barium-free microporous glass to achieve a reinforced but radiopaque composite with improved finishing qualities and to examine potential application to denture base systems.

A prototype porous gel-route-prepared glass containing 40 percent SiO_2, 30 percent ZrO_2, and 30 percent Al_2O_3 was obtained from Owens-Illinois. In a typical composite formulation the glass filler proved highly prorous. Working properties of the mix were poor. An extremely low powder/liquid ratio was required apparently because of the high porosity of the glass. Curing of the composite was very slow or sometimes did not occur. Furthermore, on addition of peroxide initiator the glass turned grayish. This apparently resulted from reaction with organic residues remaining in the glass after manufacture.

Table 20

Effect of Fluorosilane (TDOFS) Treatment of Glass Filler on 24 Hour Diametral Tensile Strength of Experimental Composites

	Liquid Formulation	Silane Treatment of Glass Filler	P/L Ratio	DTS + Std. Dev. (No. of Specimens)
A	BIS-GMA (8) IBM (2) 0.3% DHPPT	1st TDFOS 2nd A-174	3	30.0 ± 1.5 (6)
B	Same as A	1st A-174 2nd TDFOS	3	41.7 ± 2.3 (5)
C	Same as A	Only A-174	3	46.9 ± 2.3 (4)
D	BIS-GMA (85%) DMGDMA (14.7%) DHPPT (0.3%)	1st TDFOS 2nd A-174	3	29.2 ± 5.0 (5)
E	Same as D	1st A-174 2nd TDFOS	3	48.5 ± 3.9 (6)
F	Same as D	Only A-174	3	53.1 ± 2.2 (6)
G	BIS-GMA (83.7%) DMGDMA (14.8%) PDFOMA (1.2%) DHPPT (0.3%)	1st A-174 2nd TDFOS	3	47.4 ± 4.0 (6)
H	Same as G	Only A-174	3	48.4 ± 2.0 (4)
I	BIS-EDMA (49.3%) DMGDMA (41.3%) PDFOMA (9.2%) BDMA (0.2%)	1st A-174	4	48.9 ± 3.5 (5)
J	Same as I	Only A-174	4	43.2 ± 1.2 (5)

Monomers

BIS-EDMA = BIS-(2-methacryloxyethoxyl) ether of Bis phenol A
IBM = Isobornyl methacrylate
DMGDMA = decamethylene glycol dimethacrylate
PDFOMA = pentadecafluoroctyl methacrylate amine
DHPPT = N,N-bis(2-hydroxypropyl)-p-toluidine
BDMA = t-butyl-dimethylaniline

Incorporation of microporous glass to obtain a radiopaque easily polishable denture base was also investigated. From 20 to 40 percent of γ-methacryloxypropyltrimethoxysilane-treated microporous glass was incorporated into a typical denture base resin. Rectangular denture base specimens of the different materials were obtained after a 9 h cure in a denture flask at 74 °C and 0.5 h at 100 °C. The working properties of the mix were not altered by incorporation of the glass. The experimental materials were somewhat lighter in color, but all other properties were similar to current commercial material. Finish and polish of the experimental materials were very satisfactory. However, when the specimens were placed between a wedge and subjected to x-rays, the denture base showed no radiopacity on the exposed film, despite the radiopacity of the filler.

We anticipate being supplied with other microporous fillers which will be examined for these applications.

F. Improving Dental Cements

1. Vanillate-Containing Cements

Zinc oxide-eugenol (ZOE) cements, because of the excellent biocompatibility of the hardened material, have found a wide range of applications in dentistry [29,30]. They have excellent sealing characteristics and possess bacteriocidal qualities. Their limited strength and poor resistance to wear and disintegration, partially because of their relatively high solubility in oral fluids, deter their more extensive use as temporary restorations. Because the electron-rich phenolic hydroxyl group in the eugenol inhibits free radical polymerization, acrylic resins and to a lesser extent, dental composites, in contact with a ZOE cement do not polymerize completely. This incomplete cure results in polymer surface regions with poor physical properties such as low surface hardness. Furthermore, ZOE cements adhere only weakly to acrylic restorations and poorly to bone or dental tissues.

Although the eugenol incredient is relatively nontoxic, free eugenol has some inflammatory characteristics [31-35]. It has a penetrating, long-lasting odor and lingering taste which can be unpleasant to many patients. Incompletely hardened cements containing much residual eugenol can produce irritation and toxic cell reactions [36,37].

To overcome some of these deficiencies, especially to improve the mechanical strength of the ZOE cement, much research has been conducted to replace eugenol, but the use of eugenol substitutes usually results in cements possessing poor physical properties.

Zinc oxide will react with many chelate forming compounds, especially those containing o-methoxyphenol (guaiacol) groups, to yield cementitious products. Cements obtained from o-ethoxybenzoic acid (EBA) and zinc oxide have found a considerable number of applications in dentistry because of their strength and excellent biocompatibility, especially as luting agents and as bases [38,39]. However, the materials disintegrate too rapidly under clinical condition to be employed for more permanent restorations.

The initial objectives of this study were to (1) synthesize 2-methoxyphenol (guaiacol) derivatives such as 2,5-dimethoxyphenol (DMP) and esters of vanillic (4-hydroxy-3-methoxybenzoic acid) or its isomers which are liquids at room temperature, (2) study their reaction with metal oxides, and (3) evaluate the properties of the resulting cements.

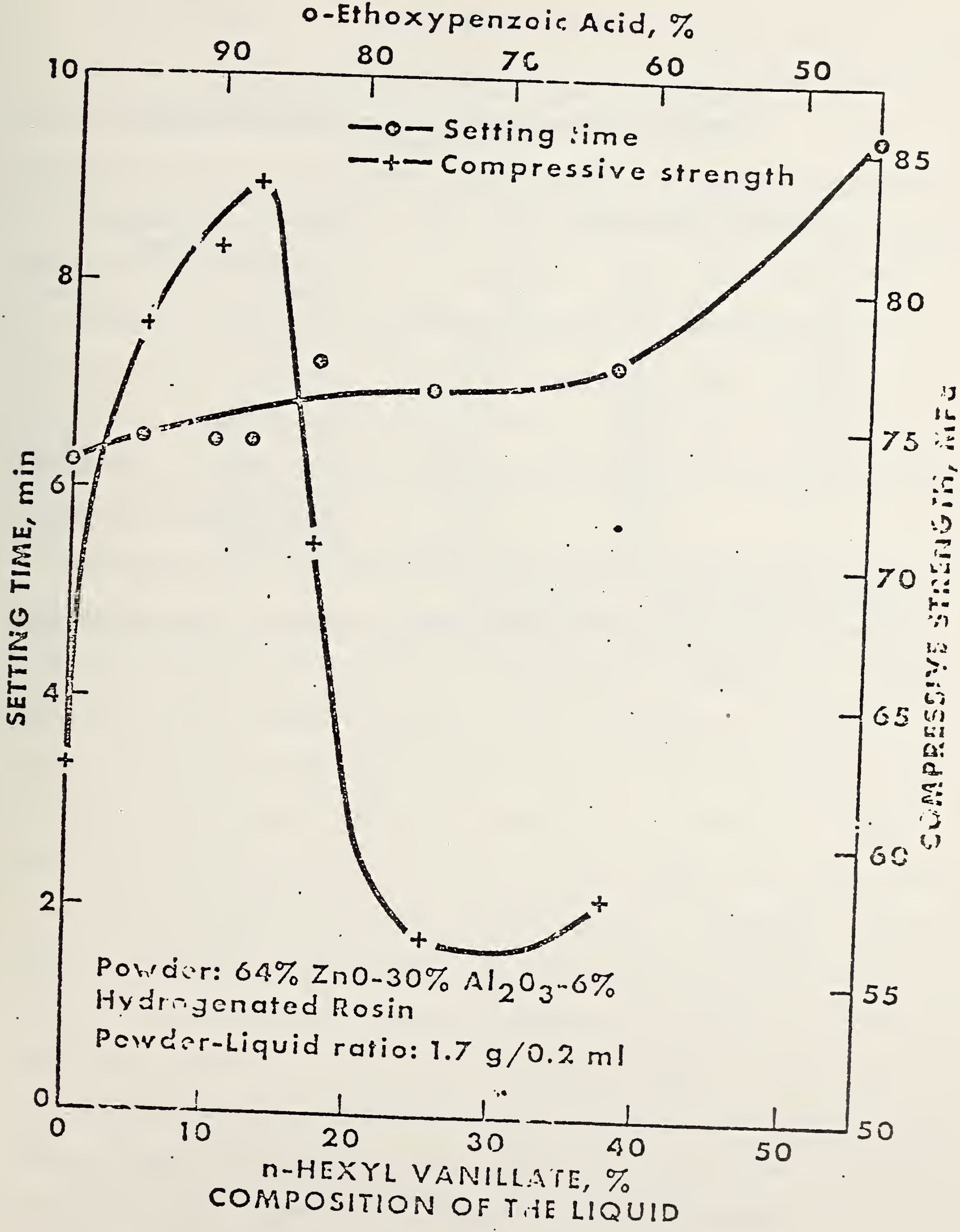
Results of the investigation of the usefulness of DMP cements were described in the previous report [1]. DMP containing cements may be useful where materials with properties intermediate to those of ZOE or EBA are desired provided DMP is as biocompatible as the structurally related eugenol.

The second phase of this effort was concerned with cements in which the liquid ingredients are esters of vanillic acids or its isomers containing o-alkoxyphenol or other groups capable of forming chelates.

Neither vanillic acid nor its common isomers are liquids at room temperature, which is a prerequisite for conveniently preparing a cement by mixing the chelator with a metal oxide. However, the hexyl ester of vanillic acid is a liquid at room temperature. Hexyl 4-hydroxy-3-methoxybenzoate (hexyl vanillate, HV) was synthesized from vanillic acid and n-hexanol [40], refluxed for 26 h and distilled under reduced pressure.

On mixing hexyl vanillate (HV) with zinc oxide (reagent grade, sieved through a No. 70 sieve) a cohesive cement is formed slowly, hardening only after several hours. More rapid curing is obtained on preparing solutions of the vanillate in another liquid chelating agent such as o-ethoxybenzoic acid. Typical results obtained with mixes containing solutions of these chelating agents with 64 percent zinc oxide, 30 percent aluminum oxide, 6 percent hydrogenated rosin powder and a powder/liquid (P/L) ratio of 1.7 g/0.2 ml are given in Table 21 and Fig. 1. The best physical properties are obtained in the 5 to 25 percent vanillate region. The cement containing 12.5 percent hexyl vanillate hardened in 6.5 min to give a one-day compressive strength of 84 MPa and a diametral tensile strength of 6.2 MPa. This compares with a one week compressive strength range of 16 to 38 MPa and a tensile strength of 1.4 to 2.5 MPa for ZOE cements [39].

PROPERTIES OF n-HEXYL VANILLATE-o-ETHOXYBENZOIC ACID-ZINC OXIDE CEMENTS



Powder: 64% ZnO-30% Al_2O_3-6% Hydrogenated Rosin

Powder-Liquid ratio: 1.7 g/0.2 ml

Figure 1

Table 21

Properties of Hexyl Vanillate-o-Ethoxybenzoic Acid Cements with Zinc Oxide-Aluminum Oxide-Hydrogenated Rosin Powders

Composition of Liquid			Properties of Cement[a]	
			Strength	
n-Hexyl Vanillate %	EBA %	Setting Time min	Compressive MPa	Tensile MPa
100	--	> 180	--	--
50	50	9.5	--	--
37.5	62.5	7.25	57.9 ± 12.7	--
25	75	7.0	56.4 ± 10.6	--
17	83	7.25	70.6 ± 10.6	5.6 ± 0.3
12.5	87.5	6.5	83.6 ± 11.0	6.2 ± 0.8
10	90	6.5	81.3 ± 12.1	--
5	95	6.5	78.4 ± 5.4	6.0 ± 1.1
0	100	6.25	62.6 ± 9.0	--

[a] Powder-liquid ratio: 1.7 g/0.2 ml
Powder: 64 percent ZnO--30 percent Al_2O_3--6 percent Hydrogenated Rosin

With different P/L ratios, compositions having varying physical properties, useful for different dental applications, can be prepared (Table 22). Depending on the consistency, mixing characteristics and film thickness desired for specific applications, the materials are useful as intermediate restoratives, insulating bases, root canal restorations, and as pulp capping and luting agents.

Generally, the larger the amount of powder incorporated per unit volume of liquid the greater was the strength and the lower the water solubility (Table 22). Too high a P/L ratio yields mixes of high consistency, which, because of poor handling characteristics, would not be suitable for clinical applications.

The powder-liquid ratio to be employed depends on the ultimate use of the cement. Thus, a material prepared by mixing 1,1 g to 1.3 g of powder with 0.2 ml liquid is suitable as a luting agent for cementation of crowns and bridges where a material having a thin film thickness is preferred. Mixes of heavier consistency (see Table 22) are useful as insulating bases, and with or without modifications, as materials for temporary fillings. Other uses of these materials are as pulp capping agents, root canal restorations, and with modifications, as impression pastes. The material properties clearly surpassed the requirements of American Dental Association Specification No. 30 for Dental Zinc Oxide-Eugenol Type Restorative Materials, Type III, Class 1 (filling materials and bases), and Type IV (cavity liners) [41]. If the powder components are sieved to give a proper film thickness in the hardened cement, these materials will significantly exceed the requirements of Type II, Class 1 cements (for permanent cementing purposes).

Comparison of data given in Table 22 shows that hexyl vanillate HV-EBA disks solubilize considerably less than disks prepared from EBA cements

TABLE 22

Properties of n-Hexyl Vanillate-EBA Cements of Varying Powder-Liquid Ratios

Powder: 64% ZnO; 30% Al_2O_3; 6% Hydrogenated Rosin

Liquid: 12.5% Hexyl Vanillate; 87.5% EBA

Powder/0.2 ml Liquid	Setting Time	Strength		Water Solubility		Consistency	Film Thickness
		Compressive	Tensile	Wt. Loss of Disk	H_2O Residue		
g	min	MPa	MPa	%	%	min	µm
2.0	6.0	88.2 ± 2.7	7.3 ± 0.4	0.28	0.01	--	--
2.0[a]	--	91.3 ± 8.2	7.8 ± 0.9	0.46	0.02	--	--
1.7	6.5	83.6 ± 11.0	6.2 ± 0.8	0.24	0.02	13.5 (120 g)[b] 21 (2500 g)[b]	184
1.3	5.5	61.4 ± 11.2	5.0 ± 0.1	0.51	0.10	31 (2500 g)[b]	--
1.1	6.0	68.6 ± 7.6	5.9 ± 0.5	0.58[c]	0.12[c]	35 (120 g)[b]	26.6

[a] Liquid: 62.5% EBA; 37.5 eugenol

[b] Load applied

[c] Water solubility of a commercial ZOE luting agent: Wt. loss of disk 3.16%; water residue: 0.02%

employing the same P/L ratio of 2.0 g/0.2 ml. Similarly, at a luting consistency, HV-EBA disks lose much less weight than those prepared from a commercial ZOE cement.

Specimens with the composition given in Table 23 were prepared according to the ADA Specification No. 30, immersed in water that was changed weekly and weighed after various time periods. The table compares solubility data for the cement specimens containing hexyl vanillate-EBA and those prepared from a commercial ZOE cement.

TABLE 23

Solubility and Disintegration of Hexyl Vanillate-EBA Cements (HV-EBA)

Powder: 64% ZnO; 30% Al_2O_3; 6% Hydrogenated Rosin

Liquid: 12.5% Hexyl Vanillate; 87.5% EBA

Powder/Liquid Ratio: 1.3 g/0.2 ml for the experimental cement; 0.67 g/0.2 ml for commercial material as recommended in the manufacturers instructions

	Average Change in Weight Percent		
Material	1 day	1 month	6 months*
HV-EBA	-0.27	0.48	0.80
ZOE†	-1.85	-3.38	-12.40

*When the water in which the specimens were stored during the last week prior to the 6-month storage period was evaporated, the weight of the solid residue was, respectively, 0.5 percent of the HV-EBA specimens and 0.8 percent of the ZOE material.

†Commonly used commercial ZOE cement.

If desirable, the setting time of the HV-EBA cements can be reduced by addition of small amounts of acid to the liquid. Table 24 shows the rapid decrease in the setting time (from 6.5 min to 20 s) of cements to which 0.1 to 10 percent acetic or acrylic acid was added. An acid capable of forming a chelate may be most suitable to reduce setting time. Thus, addition of 0.8 percent dimethylolpropionic acid to the liquid decreased setting time and improved mechanical properties of the cement.

Because of the electron poor nature of the hydroxyl group of hexyl vanillate neither this compound nor HV-EBA cements inhibit polymerization of acrylic or composites. On the other hand, the inhibiting action of eugenol or 2,5-dimethoxyphenol when added in small amounts to the catalyst paste of a commercial composite is given by Table 25. Thus, the presence of even 0.1 percent of these compounds in the composite mix yields a soft polymer even after allowing 15 min to cure. Addition of 1 or 5 percent of these phenolic compounds further retards the polymerization. In comparison neither EBA or HV in up to 5 percent concentration appreciably affect the polymerization.

TABLE 24

Effect of Acid Addition on the Properties of HV-EBA Cements

Composition: Powder: 64% ZnO; 30% Al_2O_3; 6% Hydrogenated Rosin

Liquid: 12.5% Hexyl Vanillate; 87.5% EBA

Powder/Liquid Ratio: 1.3 g/0.2 ml

Acid Added to Liquid %	Setting Time min	Strength Compressive MPa	Strength Tensile MPa
0.1 Acetic	5.5	61.4 ± 11.2	5.0 ± 0.1
0.1 Acetic	4.5	55.1 ± 17.5	--
1 Acetic	2 to 2.5	--	--
0.1 Acrylic	5	54.3 ± 14.5	--
1 Acrylic	3	40.3 ± 6.4	--
10 Acrylic	0.3	--	--
1 Benzoic	5.0	--	--
1 Polyacrylic (MW=20,000)	4	--	--
1 Polycarboxylated Polystyrene	4.5	--	--
0.8 Dimethylolpropionic	4	71.7 ± 7.1	6.4 ± 0.8
3 Hydrocinnamic	6	--	--

TABLE 25

Inhibiting Effect of Phenolic Derivatives on the Cure of a Commercial Composite

Liquid added to Composite, %[a]	Cure Time in Min of Composite Containing			
	Eugenol	o-Ethoxy-benzoic Acid	2,5 Dimethoxy-Phenol	n-Hexyl Vanillate
0	4 to 4.5	4 to 4.5	4 to 4.5	4 to 4.5
0.1	∿ 30 (soft)	4 to 4.5	∿ 15 (soft)	4 to 4.5
1	> 180	4	∿ 90 (soft)	4.5 to 5
5	> 1400	4 to 4.5	> 1400	6

[a] Phenolic derivatives were mixed into the catalyst paste. Concentration based on total weight of pastes used to prepare composite (Adaptic).

Not only is the rate of polymerization of resin that is contacted unchanged when using the newly developed cement but also the surface properties of composites cured against the newly hardened cement remain unaltered. Table 26 gives the results of indentation and recovery tests of the surface of a composite cured against HV-EBA cement which had been mixed 10 min before placing the composite. The surface hardness of composite specimens cured against the HV-ZOE cements (57.6 μm) is similar to that of composite specimens (blanks) which were not in contact with cement. However, composites cured against ZOE cement had higher indentation (63.1 μm) and lower percent recovery values indicating an inhibited (lower degree) cure (polymerization) resulting from the presence of eugenol at the resin-cement interface.

TABLE 26

Indentation and Percent Recovery of Composites Cured in Contact with Dental Cements

Cement was cured for 10 min prior to placing the composite.
Composite was stored in 100% RH for 24 h.

Composite Cured Against	Indentation[a] μm	Recovery, %[b]
--	56.9 ± 3.5	76.3 ± 4.5
ZOE Cement	63.3 ± 3.1	70.3 ± 3.9
HV-EBA Cement	57.6 ± 2.1	78.1 ± 2.8

[a] Using a 12.7 mm steel ball loaded at 30 kg for 10 min.
[b] 10 min after release of the 30 kg load.

The HV-EBA cements adhered strongly to nonprecious dental alloys and to amalgams, dental resins, and composites. Thus, nonprecious alloys or amalgam disks or rods, when cemented together with the cements and placed in water, adhered strongly. Even after 10 months storage of the specimens in water this bonding was still extremely strong. Similarly, cement disks cured against dental composite adhered strongly to the composite after 10 months storage in water. Cements based on ZOE or EBA do not bond to such substrates to any appreciable extent. A weaker bond is formed between the HV-EBA cement and gold. The strong adhesion of the cement, especially to resins and nonprecious alloys, should prove most useful for clinical applications where a strong cement-resin bond is desired.

The complete absence of inhibition of HV-ZOE cements coupled with their excellent adhesion to resins and metals is advantageous and should make it possible to place acrylic resins or composites over bases employing this cement. Furthermore, a portion of the cement when used clinically as a temporary restoration can be retained as a base for an acrylic resin restoration. A complete reexposure of deep cavities is avoided, reducing irritation of the dental tissues during this procedure.

HV-EBA cements have no odor. The presence of the vanillate esters should yield cements with bacteriocidal properties. Although hexyl vanillate has been considered as a food preservative, the toxicological and biocompatible properties of the newly developed cements must be studied further before its dental usefulness can be ascertained.

It is possible to improve the properties of the HV-EBA cements in many ways. Investigations conducted so far have been directed toward (1) determining the scope of the reaction of vanillate-EBA with ZnO, and (2) modifying the properties by incorporation of polymeric reinforcing agents and addition of polymerizable compounds and reinforcing fillers to the formulations.

Replacing hexyl vanillate with other esters of vanillic acid yielded cements with properties similar to those employing hexyl vanillate. However, these cements may possess specific properties such as increased hydrophobicity which makes the hardened material more desirable for specific applications in dentistry where water repellancy and minimum solubility of the material in the mouth's fluids is of prime importance. The n-heptyl, _n_-decyl, and 2-ethylhexyl vanillate and hexyl isovanillate were synthesized. The heptyl vanillate, synthesized by a procedure similar to that described for the hexyl compound, has a boiling point of 181 to 183 °C at 2 mm pressure and a melting point at 24.5 to 30 °C. (Yield: 70 percent.)

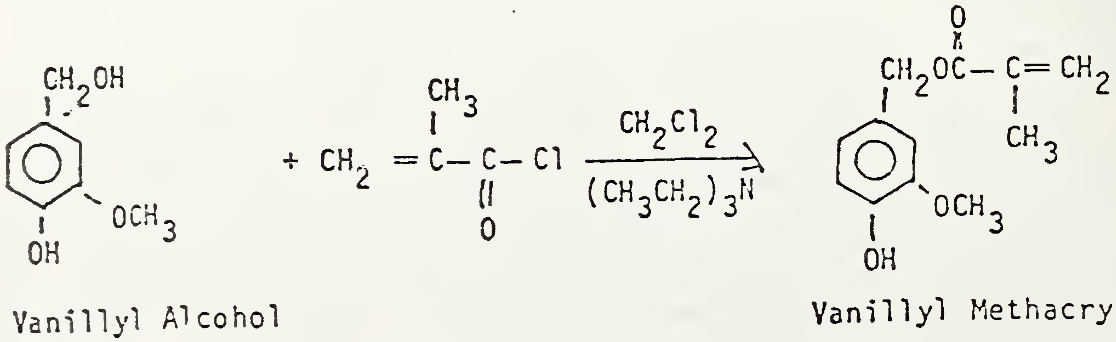
The _n_-decyl vanillate was synthesized by refluxing decyl alcohol with vanillic acid in the presence of _p_-toluenesulfonic acid. After removal of the unreacted alcohol, purification, and recrystallization from _n_-pentane, the _n_-decyl vanillate had a melting point of 40 to 40.5 °C. (Yield: about 50 percent.)

2-Ethylhexyl vanillate was prepared from the corresponding, dry alcohol (13.0 g, 0.10 mol), vanillic acid (8.4 g, 0.05 mol), and 0.1 g p-toluenesulfonic acid. After refluxing for 27 h and extraction with $NaHCO_3$ and H_2O the product distilled at 192 to 193 °C at 2 mm. The slightly yellow viscous liquid was 98 to 98.5 percent (gas chromatography) pure. (Yield: 97 percent.)

n-Hexyl isovanillate was obtained on refluxing n-hexanol (dried over molecular sieve), 10.2 g (0.1 mol), isovanillic acid (3-hydroxy-4-methoxybenzoic acid, 8.4 g, 0.05 mol), 0.1 g p-toluenesulfonic acid, and 100 ml toluene for 24 h. Most of the solvent was distilled off, another 0.1 mol alcohol and xylene were added, and the mixture was refluxed an additional 10 h. The unreacted acid was filtered off. After addition of methylene chloride, and extraction with $NaHCO_3$, the organic layer was dried and distilled. The n-hexyl isovanillate distilled at 173 °C/2.5 mm. The slightly viscous, yellow liquid proved 97 to 98 percent pure by gas chromatographic analysis. (Yield: 59 percent.)

Properties of cements containing 1.3 g of powder mixed with 0.2 ml liquid having the same mole percentage of the respective vanillate and EBA are given in Table 27.

Another vanillyl containing compound, vanillyl methacrylate, was synthesized by the method shown below:



Vanillyl Alcohol

Vanillyl Methacrylate

TABLE 27

Properties of Cements Containing Various Vanillate Esters and EBA in the Liquid

Powder: 64% ZnO; 30% Al_2O_3; 6% Hydrogenated Rosin

Powder/Liquid Ratio: 1.3 g/0.2 ml

Liquid		Setting Time	Strength, MPa	
Vanillate	EBA	min	Compressive	Tensile
12.5%-_n_-Hexyl[*]	87.5%	5.5	61.4 ± 11.2	5.0 ± 0.1
13.2 _n_-Heptyl[*]		5.5	58.3 ± 11.3	6.3 ± 0.8
12.3% _n_-Decyl	87.7%	5.0	41.5 ± 11.9	--
15.3% _n_-Decyl[*]	84.7%	4.5	50.1 ± 5.2	5.6 ± 0.4
18.3% _n_-Decyl	81.7%	5.0	42.6 ± 7.0	--
13.9% 2-Ethylhexyl[*]	86.1%	5.5	48.5 ± 4.2	5.6 ± 0.5
12.5% _n_-Hexyl[*†]	87.5%	5.0	55.1 ± 9.4	6.5 ± 1.2

[*] Equimolar composition of vanillate in the liquid

[†] Isovanillate

The colorless liquid product, b.p. 160 to 170°/4 mm, n_d^{22} = 1.5313 was characterized by gas chromatographic (GLC) and infrared (IR) analyses. GLC analysis indicated the presence of some impurities ($\sim$ 5 percent) in this monomer. Because of the greater electron densities of the aromatic rings of both vanillyl alcohol and its methacrylate derivative compared to vanillic acid or its hexyl ester (HV), greater inhibition of the resin polymerization was anticipated. Neat vanillyl methacrylate did not polymerize within one hour using an initiator system consisting of 1 percent benzoyl peroxide and 0.5 percent N,N-dimethyl-3,5-xylidine. However, vanillyl methacrylate did photocure in less than 2 min with 0.5 percent benzoin ethyl ether and UV radiation (Nuvalite). Therefore, it may be possible to employ vanillyl methacrylate in photocurable cement.

Polymeric reinforcing agents can be incorporated in either the liquid or the powder. A number of rubbery polymers were dissolved in the liquid. Alternatively, small particle size polymers were incorporated in the powder resulting in cements having properties given in Table 28. Thus, less brittle materials with improved tensile and compressive strength especially useful as temporary restoratives can be prepared by addition of various polymeric reinforcing agents to the powder or liquid.

Investigations were initiated to take advantage of the unique behavior of these cements in not inhibiting polymerization. Thus, monomeric liquids such as 1,10-decamethylene glycol dimethacrylate containing an amine accelerator were prepared and mixed with powder containing peroxide initiator. This addition of monomer improved the physical properties of the cement.

TABLE 28

Composition--Powder: 64% ZnO; 30% Al_2O_3; 6% Hydrogenated Rosin

--Liquid: 12.5% Hexyl Vanillate; 87.5% EBA plus polymer additive dissolved in liquid.

P/L Ratio: 1.3 g/0.2 ml liquid.

Polymer Additive	Setting Time min	Strength, MPa Compressive	Tensile
None	5.5	61	5.0
2% Polyurethan (Estane 5712, B. F. Goodrich)	5.0	65	5.7
3% Butadiene-acrylonitrile, vinyl terminated (Hycar 1300 X-22, B. F. Goodrich)	6.0 to 6.5	61	5.7
10% Methacrylate copolymer (Acryloid K 120N, Rohm and Haas)†	4.0	31	6.6
10% Vinylite VYHH (Union Carbide)†	6.0 to 6.6	76	8.2

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† Added to the polymer powder

As an example the powder was thoroughly mixed with 0.1 percent finely powdered benzoyl peroxide.

To the liquid containing 12.5% hexyl vanillate--87.5 percent EBA was added 10 percent of 1,10-decamethylene glycol dimethacrylate containing 0.5 percent p-(dimethylamino)phenthanol accelerator.

The powder and liquid were mixed employing 1.3 g of powder per 0.2 ml liquid. The material hardened in 6 min giving a cement with compressive strength of 79.4 ± 1.8 MPa and a tensile strength of 6.3 ± 0.8 MPa.

Cementitious restoratives with drastically improved mechanical properties which could find applications as long-lasting temporary restoratives were prepared by incorporating glass or silica fillers along with the metal oxides into these formulations. Thus, in preliminary studies a powder was prepared from 64 percent zinc oxide, 30 percent aluminum oxide, and 6 percent hydrogenated rosin. Two parts of this powder were mixed with 1 part glass (Corning Glass 7724) silanized with 3-methacryloxypropyl-trimethoxysilane which had been coated with 1 percent benzoyl peroxide. The liquid consisted of a mixture of 1 part of 12.5 percent hexyl vanillate; 87.5 percent EBA, and 1 part 1,10-decamethylene glycol dimethacrylate containing 0.5 percent p-(dimethylamino)phenylacetic acid.

The powder and liquid were mixed in a ratio of 1.8 g powder per 0.2 ml liquid. The material hardened in 6 min to give a cement with a compressive strength of 137.6 ± 5.8 MPa, and a tensile strength of 14.1 MPa. Thus, the mechanical strength of these materials was about three times that of ZOE cements.

Future investigations will use different monomers and monomer concentrations as well as different amounts of glass fillers to optimize properties of these promising materials. Furthermore, it will be necessary to establish

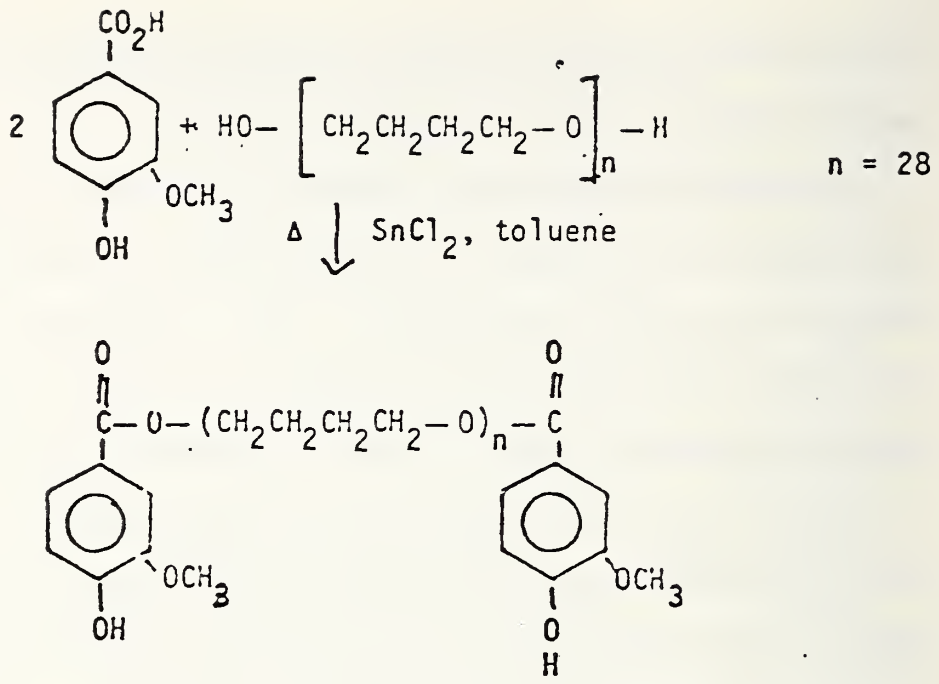
if formulations containing monomeric methacrylates can be used in deep cavities without causing inflammatory responses.

An attempt has been made to synthesize a number of divanillates. These compounds are capable of forming chelates with metal oxides at two different sites within the molecule. Thus, such compounds are potential crosslinking agents which may strengthen the phyical properties of dental cements based on the reaction of metal oxides with chelating agents.

Divanillates can be prepared from the corresponding diols and vanillic acid using methods described previously involving the synthesis of vanillic esters. Thus, 1,10-decamethylene divanillate was prepared from 1,10-decanediol (0.025 mol) and vanillic acid (0.063 mol) in the presence of 0.25 g p-toluenesulfonic acid. The mixture, dissolved in 50 ml toluene and 40 ml tetrahydrofurane, was refluxed for 30 h and stripped of solvent. The residue was purified by extraction with base. The dark brown oil was dissolved in methanol and boiled with activated carbon to remove impurities. The diester was characterized by infrared and GLC analyses and appeared to be 95 percent pure.

1.3 g of powder of the composition given previously was mixed with 0.2 ml of liquid containing 11 percent 1,10-decamethylene divanillate and 89 percent EBA (equal to the molar composition of the liquid used previously). The mix hardened in 4.5 min to give a cement with compressive strength of 70.6 MPa and a tensile strength of 7.5 MPa.

Similarly, 1,6-hexamethylene divanillate was synthesized and incorporated into the liquid. The resulting mix hardened in 5 min and had a compressive strength of 47.8 ± 3.8 MPa and tensile strength of 6.2 ± 0.8 MPa. Polymeg 2000, an oligomeric diol was used in the esterification reaction of this alcohol with vanillic acid as shown below:



The product obtained by this reaction was a waxy solid, m.p. = 28 °C, yield 65 percent, and was characterized by IR analysis.

A cement formulation was prepared by dissolving 12.5 percent polymeg divanillate in EBA. Cement specimens had approximately 2/3 the compressive strength of HV-EBA cement specimens. A cement formulation using only a small amount of the polymeg divanillate in the HV-EBA liquid gave a compressive strength value of 57.1 ± 5.9 MPa.

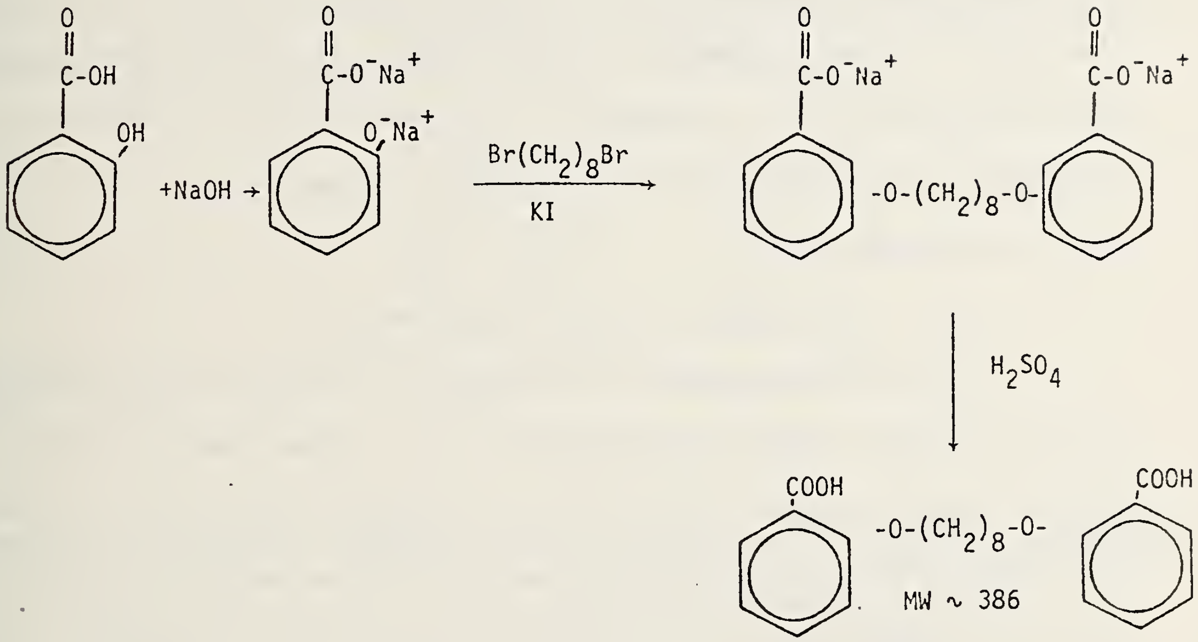
In the reaction of 1,2-propanediol and vanillic acid the primary hydroxyl group of 1,2-propanediol reacted preferentially (IR analysis) so that the actual product, a viscous yellow oil, is the monovanillate

An attempt was also made to synthesize the trivanillate ester of trimethylolpropane, but the desired product proved difficult to purify.

Two other compounds which could react with metal oxides to yield chelates were also synthesized:

1. 1,8-Bis(o-carboxy phenoxy)octane was prepared.

Synthesis of 1,8-Bis(o-carboxy phenoxy)octane



The compound was synthesized from 0.2 mole salicylic acid, 0.1 mole 1,8-dibromo-octane, 0.4 mol NaOH and potassium iodide. The mixture was refluxed in ethanol. After removal of solvent and purification an impure product was obtained, MP = 132 to 142 °C.

The compound, dissolved in EBA and mixing with the ZnO powder formed a rather brittle cement in 5 min.

2. Sebacyl di(dimethylolpropionic acid) was synthesized from 0.025 mole sebacyl chloride, 0.05 mole dimethylolpropionic acid and 0.055 mole triethylamine at room temperature. Addition of 5 percent of the purified acid to 12.5 percent HV; 87.5 percent EBA liquid and addition of the ZnO powder gave

a cement in 5 min which had properties (compressive strength 55.4 ± 6.5 MPa, tensile strength 5.1 ± 0.4 MPa) very similar to HV-EBA cement not containing the sebacyl di(dimethylolpropionic acid).

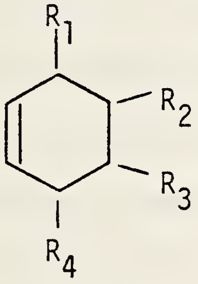
Because of the potential usefulness of these noneugenol, nonpolymerization-inhibiting, high strength cements developed during the year, a "patent disclosure" has been prepared. A talk "Cements from 2,5-Dimethoxyphenol and Zinc Oxide" by J. W. Stansbury, H. Argentar, and G. M. Brauer was presented at the annual meeting of the International Association for Dental Research, Chicago, 1981.

2. New Polybasic Acid-Derived Cements

The resinous nature of certain salts derived from both monocarboxylic (e.g. abietic acid) and dicarboxylic (e.g., dimer sebacic acid) acids has been known for some time [42-44]. The preparation of well defined polyvalent metallic dicarboxylates such as calcium sebacate usually requires either high temperature (fusion reaction) or solution (metathesis reaction) techniques which are probably not suitable to the usual dental clinical situation for the preparation of cements.

Since the solid phase reaction at ambient temperature between the relatively high melting typical organic diacids (e.g., sebacic acid, m.p. 133 °C) and the still higher melting basic polyvalent metallic compounds (e.g., $Ca(OH)_2$, m.p. 580 °C) is likely to be extremely slow, this route to polycarboxylate cements is precluded. A solution technique, while feasible, would have to contend with the presence of solvent (e.g., H_2O) molecules and other byproducts in the structure which would tend to weaken the polycarboxylate cement.

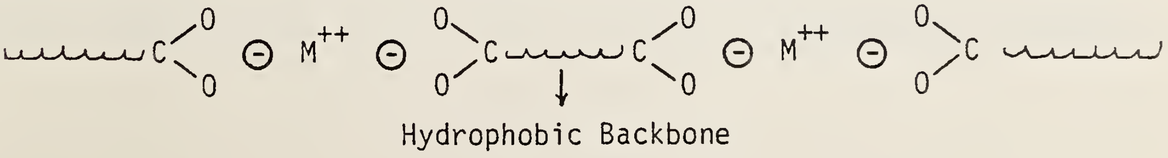
Dimer acids, a complex isomeric mixture of 36-carbon diacids with smaller amounts of 54-carbon tribasic acids and trace amounts of 18-carbon monobasic monomer acid, is a unique polybasic acid in its hydrophobic character and room-temperature liquidity. The principal chemical structural feature of dimer acids is that of a tetrasubstituted cyclohexene dicarboxylic acid. A simplified representation of dimer acids is as follows:



where the R groups are long chain alkyl groups, two of which are terminated by carboxyl groups (e.g., $R_1 = (CH_2)_8\ CO_2H$, $R_2 = CH{=}CH(CH_2)_8\ CO_2H$, $R_3 = CH_3(CH_2)_4$-, and $R_4 = CH_3(CH_2)_7$- etc.).

The conventional polycarboxylate dental cements are based on the reaction of a liquid form of a polymeric poly acid (e.g., polyacrylic acid in an aqueous solution) with a solid basic inorganic phase (e.g., zinc oxide, etc.) to give a polycarboxylate polymer. In this case, the polycarboxylate reaction crosslinks the polymer and aids in its adhesion to tooth structure. A drawback of this useful dental material is its hydrophilicity.

Polycarboxylates that are formed from dimer acids and divalent metals are linear polymers having carboxylate linkages in their backbone as depicted in a simplified fashion below:



In the past, such polymers have been prepared by fusion or methathesis [42].

We have initiated a study to determine the feasibility of preparing such polycarboxylate polymers, termed halatopolymers, by direct reaction of the liquid dimer acid with basic polyvalent salts such as $Ca(OH)_2$. Preliminary results using powdered $Ca(OH)_2$ and a highly pure dimer acid have been encouraging. A hard, white cementious material was obtained in about 2 min at 37 °C and 100 percent relative humidity from mixing 2 parts by weight of $Ca(OH)_2$ with 1 part by weight of dimer acid. A 1:1 powder/liquid ratio gave a somewhat more flexible cement in about in about 4 min at 37 °C and 100 percent relative humidity. Other salts of calcium such as the carbonate and the various phosphates did not react under these conditions. However, mixtures of these salts with various amounts of $Ca(OH)_2$ did form hard masses in reasonable setting times.

Since the conventional polycarboxylate cements display good adhesive properties, it will be interesting to see if the dimer acid cements have similar properties with respect to hard tooth tissue. The dimer acid cements may not be as hygroscopic as the conventional polycarboxylate cements due to the relatively low concentration of carboxylate groups in a basically hydrophobic hydrocarbon structure.

3. Polyvinyl Phosphonic Acid Cements

There is extensive literature concerning the ability of polyphosphonic acids to strongly complex with tooth structure. [45-49] Addition of a polymeric phosphate acid to a zinc phosphate and a polycarboxylate cement improved their mechanical properties and adhesion to tooth structure [50].

A review of possible alternatives to polycarboxylic acids for use in dental cements reveals that polyphosphonates are feasible ones. Since polyvinyl phosphonic acid is a strong acid and forms strong complexes with apatitic surfaces, cements made with it should be adhesive and more insoluble than polycarboxylic acid cements. Polyvinyl phosphonic acid greatly reduces the solubility of enamel and dentin in acid and the cement will therefore be caries inhibiting. It will also be biologically bland in dental applications because complexation with metal ions will prevent diffusion of acid into the pulp, similar to polycarboxylate cements.

The objective of this work was to produce a cement using aqueous polyvinyl phosphonic acid as the liquid and examine its properties.

Initially, polymerizations of vinyl phosphonic acid using 0.5 percent azo bis isobutyronitrile (AIBN) initiator at 70 °C for 5 h resulted in a polymer whose molecular weight was too great to give a workable mix. Therefore, it was polymerized with 2 percent AIBN at 65 °C for 2 h, and a lower molecular weight was obtained. A 75 percent aqueous solution of this polymer reacted very rapidly with available zinc oxide or silicate powders. An attempt to deactivate zinc oxide by heating at 1000 °C for 5 h did not reduce its reactivity significantly. However, after washing silicate powder for 5 min with 10 percent phosphoric acid, filtering, washing with distilled water, refiltering and drying, the product gave a workable cement.

At a powder/liquid ratio of 1.5/1 the cement had a compressive strength of 55 MPa. With further work this could undoubtedly be bettered. Unfortunately, the cement showed no adhesion to tooth structure, even when the tooth surface was primed with the cement liquid, or the cement was mixed at a powder/liquid ratio of 1.2/1 to provide more available polymer for bonding.

The bond strength of a cement may depend on the polyacid used. For example, co-polymerization of polyacrylic acid with itaconic acid for use in glass-ionomer cements reduces the bond strength. Polyitaconic acid will form a satisfactory cement but it is not adhesive to tooth structure [51].

Investigation of the bonding ability of cements made from different polyacids should give valuable information on the mechanism of bonding and factors which affect it. Polyvinyl phosphonic acid cements need to be studied further.

II. Development of Adhesive Bonding Techniques*

A. Mineralization of Dentin as an Adhesive - Developing Technique

Since the introduction of hypermineralization as a method of modifying the dentin surface to improve the adhesion of polycarboxylate cement [52] the approach has been found to benefit the bonding of composites alone [53], or in conjunction with surface active co-monomers [54] or cyanoacrylates [55]. Clinically feasible mineralizing agents have been developed which are effective with polycarboxylate cements after application for less than 3 mins. [56,57].

Commercially available cements containing a polycarboxylic acid (polycarboxylate and glass ionomer) are continually changing and, unfortunately, the effect of a given mineralizing agent varies with the particular formulation of each product. [58,59] This suggests that the cations in the cement play a major role.in adhesion. [59] Since the adhesion of polycarboxylic acid cements is essentially via ionic interaction of carboxylate anions to metal cations on the tooth surface, the adsorption, exchange or deposition of metal ions other than calcium or their salts on dentin may be beneficial. A study by Beech [60] found that pretreatment of dentin with a range of metal salt solutions gave no improvement in the bond strengths of polycarboxylic acid cements. However, sequential application of 1 M $CaCl_2$ and 0.5 M Na_3PO_4 ($Ca_3(PO_4)_2$ precipitation) for 3 min. increased the bond strength of polycarboxylate cement but not glass-ionomer.

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* Acknowledgement is given for the contribution of Dr. Derrick R. Beech, Director, Australian Dental Standards Laboratory who participated as a Guest Worker at NBS in FY 81.

The overall object of the current work was to enhance the bonding of polycarboxylate and glass ionomer cements and of self-curing monomers such as cyanoacrylates and methacrylates, by increasing the mineral content of the dentin surface or by changing its ionic character. Specific objectives were, to further investigate the in situ precipitation technique using a range of metal ions, as well as utilizing other methods of depositing cations to find a way of improving the bond strength of all polycarboxylic acid cements.

Bond strengths for the materials examined (Table 28) were determined by a method first reported by Beech (52). Briefly, a circular area (3 mm in diameter) of flat dentin or enamel surfaces of human teeth mounted in self-curing resin was masked off. An orthodontic button was cemented thereon in place and, after 24 hrs. storage in water, the load required to pull the button free was determined. The results are summarized in Tables 29-31 and in the SEM pictures of Fig. 2-13. For the latter, treated dentin sections were coated with gold/palladium and examined in a Cambridge or ETEL SEM.

The original formulation of polycarboxylate cement containing zinc oxide and perhaps some magnesium oxide in the powder typically had bond strengths to enamel and dentin of 5 and 2.5 MPa, respectively (Table 30, Poly C). Incorporation of 8% stannous fluoride in Durelon gave bond strengths for enamel and dentine of 5.8 and 4.5 MPa, respectively, in previous work reported by Beech [60]. The present work has found 6.3 and 5.2 MPa for Durelon (Table 29). The tensile strength of the cement is only around 6 MPa so these bond strengths are approaching the upper limit. Nevertheless, the calcium phosphate precipitation technique does produce a worthwhile improvement with Durelon and Poly C. It is effective after application for only 1 min. Other precipitated metal phosphates generally produced a slight decrease in bond strength with Durelon, except $Sn_3(PO_4)_2$ and $Zn_3(PO_4)_2$ (Table 29). The latter leaves the bond strengths unaffected, whereas the former appears as effective as $Ca_3(PO_4)_2$ precipitation. Zn^{++} and Sn^{++} are present in Durelon powder and these may assist in bonding to like ions. Sn^{++} also is known to have a special affinity for hydroxyapatite. $Sn_3(PO_4)_2$ did not improve the bond strength of Poly C (Table 30). Presumably Sn^{++} ions must be present in the cement to equilibrate with those on the surface. If Sn^{++} is not in the cement, the Sn^{++} on the tooth surface will diffuse into the cement and any benefit will be lost.

Methods of depositing mineral suggested by Drs. Chow and Brown (Table 29) probably could be made to work in a 1-3 min. time period. Ferric oxalate, as suggested by Dr. Bowen, has some potential with glass ionomer cement, particularly when mixed with polyacrylic acid (Table 30). The SEM of a ferric oxalate treated surface, Fig. 3, was notably different from the control (Fig. 2). It is difficult to improve glass ionomer cement bond strengths [60]. Glass-ionomer cements experience considerable ionic migration during their 24 hr. setting period, which may nullify the effect of most surface treatments by removing ions deposited on the dentin surface. Contrary to the claims of Shalaby *et al*. [61], 50% ferric chloride application after citric acid pretreatment was not beneficial to the bonding of Fuji glass-ionomer.

It was generally found that *in situ* precipitations (Fig. 5) did not alter surface morphology compared to the controls (Fig. 2 and Fig. 4) although residual precipitate was sometimes found. The treatments examined in Figs. 6-13 gave varied surface appearances, with occlusion of the ends of the tubules in many cases. Crystal growth was evident after ferric chloride treatment (Fig. 13), despite washing.

TABLE 28

Polycarboxylate and Glass - Ionomer Materials

Type	Name	Manufacturer	Powder/Liquid Ratio
Fluoridated Polycarboxylate	Durelon	ESPA	1.5:1
Polycarboxylate	Poly C	De Trey	1.5:1
Glass-Ionomer	Fuji Ionomer Type I	G. C. Chemical	1.4:1

TABLE 29

Durelon Polycarboxylate Cement

Treatment	Substrate	No.of Specimens	Mean Bond Strength ± SD (MPa)	
None	Dentin	7	5.3 ± 1.61)	
		4	5.6 ± 0.82)	5.16 ± 1.23
		6	4.37 ± 0.89)	
		6	5.49 ± 1.15)	
			[4.5 ± 1.1]**	
None	Enamel	4	4.3 ± 1.09*	
		6	3.02 ± 0.6 *	
		6	5.04 ± 1.73)	
		6	6.60 ± 1.84)	6.24 ± 1.93
		6	7.20 ± 1.97)	
			[5.8 ± 1.5]**	
Slurry of Ca Phosphates - 3 min (W. Brown)				
+ OHAP	Dentin	6	3.44 ± 0.47	
+ NaF	"	6	4.14 ± 0.78	
$CaHPO_4 \cdot 2H_2O$ forming solution - 3 min (L. Chow)	"	6	2.99 ± 1.15	
Ferric oxalate - 1 min (R. Bowen)				
A600-33 (6%)	"	6	4.74 ± 1.01	
A600-38 (4%)	"	6	2.06 ± 0.48	
A600-34 (12.6%)	"	6	4.87 ± 1.64	
6% Ferric oxalate + polyacrylic acid - 1 min	"	5	5.54 ± 2.50)	5.40 ± 2.40
1M $CaCl_2$ + 0.5M Na_3PO_4	"	6	5.26 ± 2.47)	
3 min	"	6	6.65 ± 1.9)	
	"	6	5.44 ± 1.04)	6.67 ± 2.05
	"	6	7.92 ± 2.36)	
1 min	"	6	6.1 ± 2.33	
30 sec	"	6	5.85 ± 1.28	
1M $CuCl_2$ + 0.5M Na_3PO_4 (3 min)	"	6	3.86 ± 0.94	
1M $ZnCl_2$ + 0.5M Na_3PO_4 (3 min)	"	6	5.5 ± 1.57)	5.17 ± 1.83
	"	6	4.88 ± 2.16)	
1M $MgCl_2$ + 0.5M Na_3PO_4 (3 min)	"	6	3.63 ± 0.90	
1M $SnCl_2$ + 0.5M Na_3PO_4 (3 min)	"	6	6.19 ± 1.69)	6.55 ± 1.78
	"	6	6.91 ± 1.96)	
1M $BaCl_2$ + 0.5M Na_3PO_4 (3 min)	"	6	1.58 ± 0.6	
1M $FeCl_2$ + 0.5M Na_3PO_4 (3 min)	"	6	3.89 ± 0.65	
0.5M $CrOHSO_4$ (3 min) Fresh	"	6	1.44 ± 0.55	
1M $CrOHSO_4$ (3 min) Old	"	6	2.39 ± 0.83	
15% $FeCl_3$ + 0.5M Na_3PO_4 (3 min)	"	6	1.89 ± 0.46	

* Results for enamel anomalously low compared to previous work

** Values from previous work

TABLE 30

Poly C Polycarboxylate Cement

Treatment	Substrate	No.of Specimens	Mean Bond Strength ± SD (MPa)	
None	Enamel	6	4.19 ± 1.11)	4.59 ± 0.97
	"	5	5.08 ± 0.53)	
None	Dentin	6	1.79 ± 1.01)	2.23 ± 1.10
	"	6	2.76 ± 1.03)	
1M $SnCl_2$ + 0.5M Na_3PO_4 (3 min)	"	6	1.51 ± 0.97	
1M $ZnCl_2$ + 0.5M Na_3PO_4 (3 min)	"	6	1.76 ± 0.68	
1M $CaCl_2$ + 0.5M Na_3PO_4 (3 min)	"	5	3.4 ± 1.07)	3.23 ± 1.00
"	"	6	3.09 ± 1.04)	
" (1 min)	"	5	3.20 ± 0.58	
"		6	3.61 ± 1.30	
6% Ferric oxalate + poly-acrylic acid (3 min)	"	6	2.19 ± 1.68	
"	"	6	1.94 ± 1.89	

TABLE 31

Fuji Glass-Ionomer Cement

Treatment	Substrate	No. of Specimens	Mean Bond Strength ± SD (MPa)	
None	Enamel	6	5.58 ± 1.8)	5.22 ± 1.62
		6	4.85 ± 1.5)	
			[4.5 ± 1.5]*	
None	Dentin	6	2.73 ± 0.83)	2.40 ± 0.83
		5	2.0 ± 0.72)	
			[2.5 ± 1.6]*	
Ferric Oxalate (R.Bowen)				
6%:1 min	"	6	2.93 ± 0.4	
12.6%:3 min	"	5	3.0 ± 0.24	
6% Ferric oxalate + polyacrylic acid (3 min)	"	6	3.41 ± 1.0)	3.37 ± 1.51
"	"	6	3.34 ± 1.93)	
1M $Al(NO_3)_3$ + 0.5M Na_3PO_4 (3 min)	"	6	2.28 ± 1.18	
1M $SnCl_2$ + 0.5M Na_3PO_4 (3 min)	"	6	2.61 ± 0.16	
1M $ZnCl_2$ + 0.5M Na_3PO_4 (3 min)	"	5	1.54 ± 0.79	
15% $FeCl_3$ (1 min)	"	5	1.31 ± 0.3	
50% citric acid (1 min) then 15% $FeCl_3$ (1 min)	"	6	1.72 ± 1.18	
15% $FeCl_3$ + 0.5M Na_3PO_4 (3 min)	"	6	1.50 ± 0.89	

Fig. 2 Dentin as polished (control) x 600

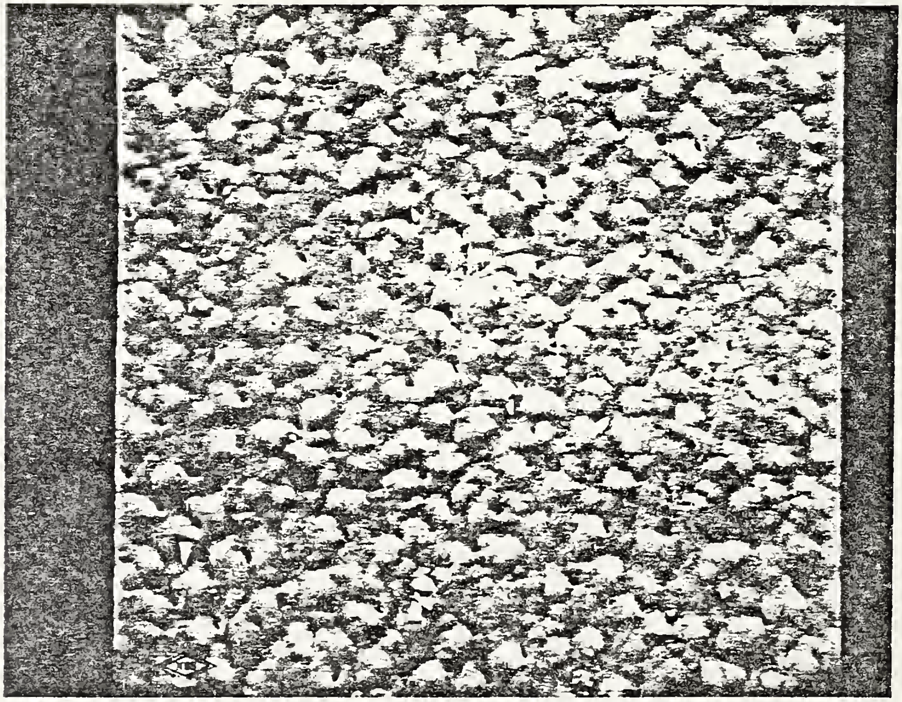

Fig. 3. Dentin 6.7% ferric oxalate (1 min) x 500

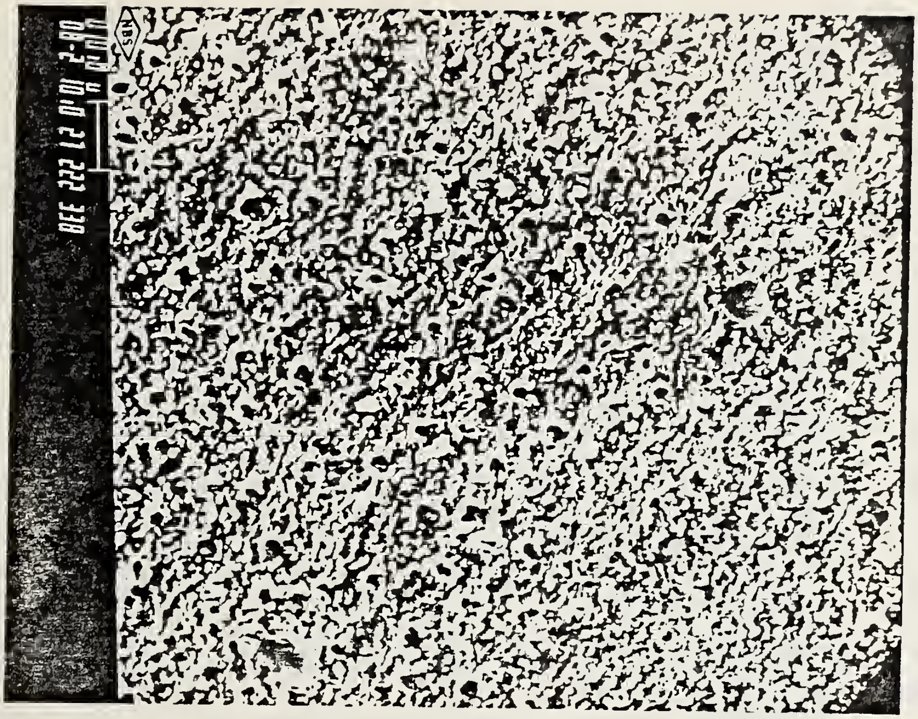

Fig. 4 Dentin. 1 min citric acid (control)

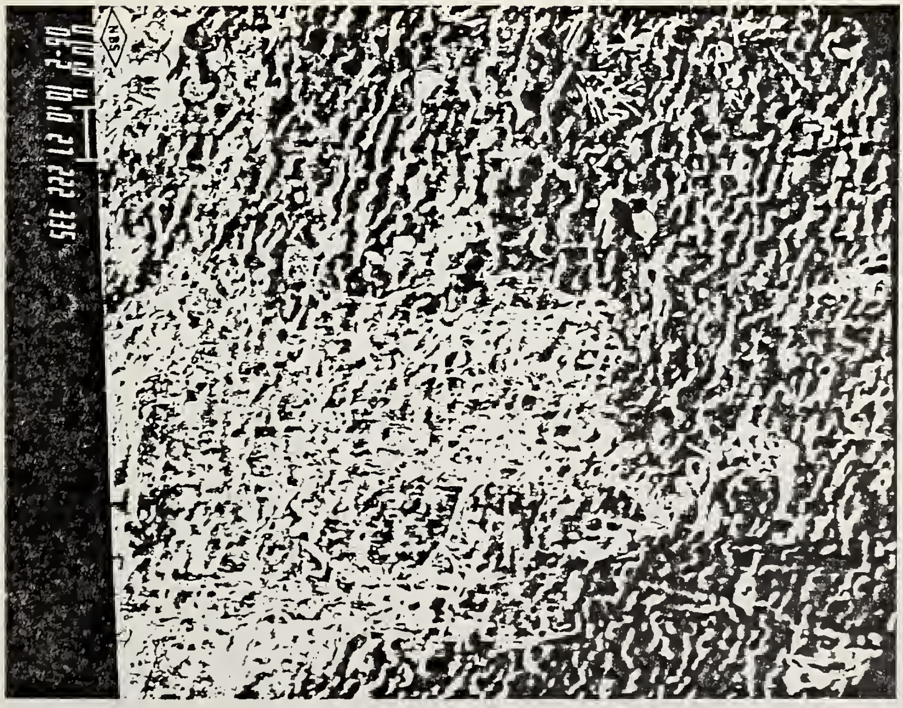

Fig. 5 Dentin. 1 min citric acid then 1M $CaCL_2$+0.5M Na_3PO_4 (3 min)

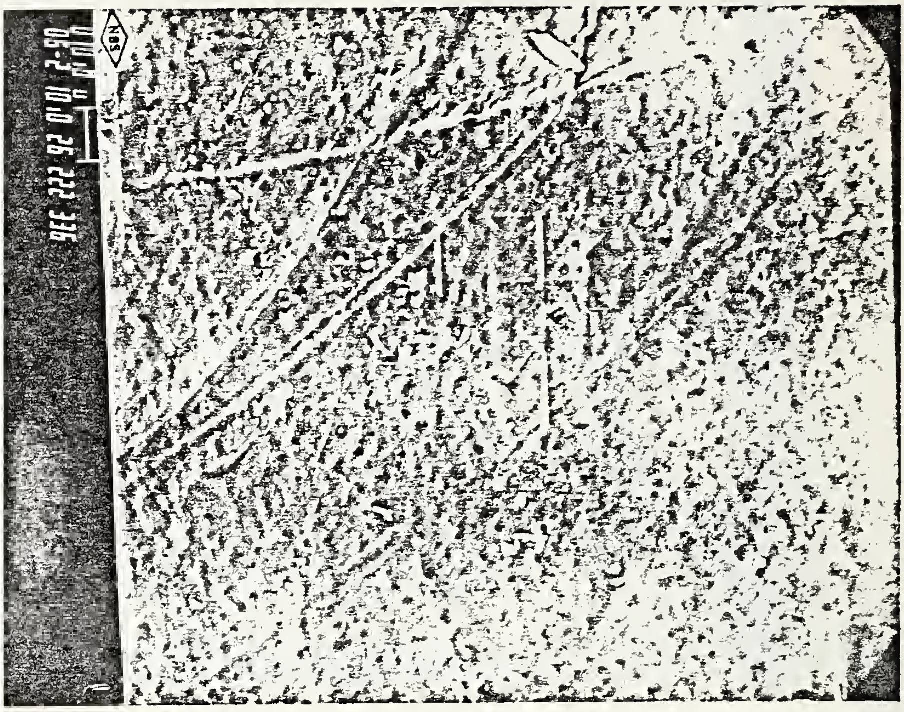

Fig. 6 Dentin. 1 min citric acid then 6.7% ferric oxalate (1 min

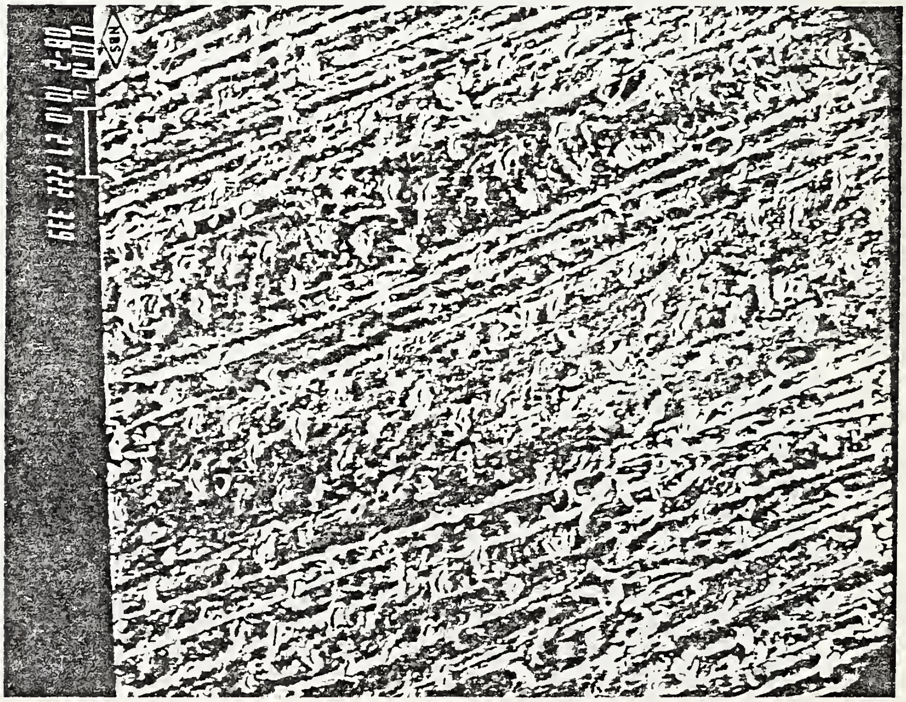

Fig. 7 Dentin. 1 min citric acid then 1M $CaCl_3$ (3 min)

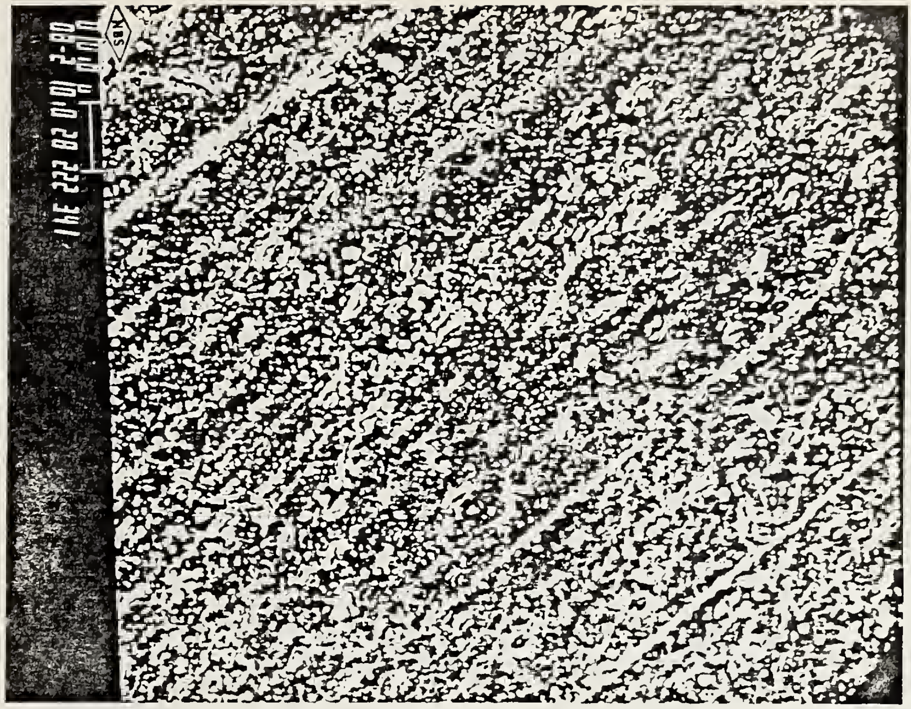

Fig. 8 Dentin. 1 min citric acid then 6.7% ferric oxalate + polyacrylic acid (3 min)

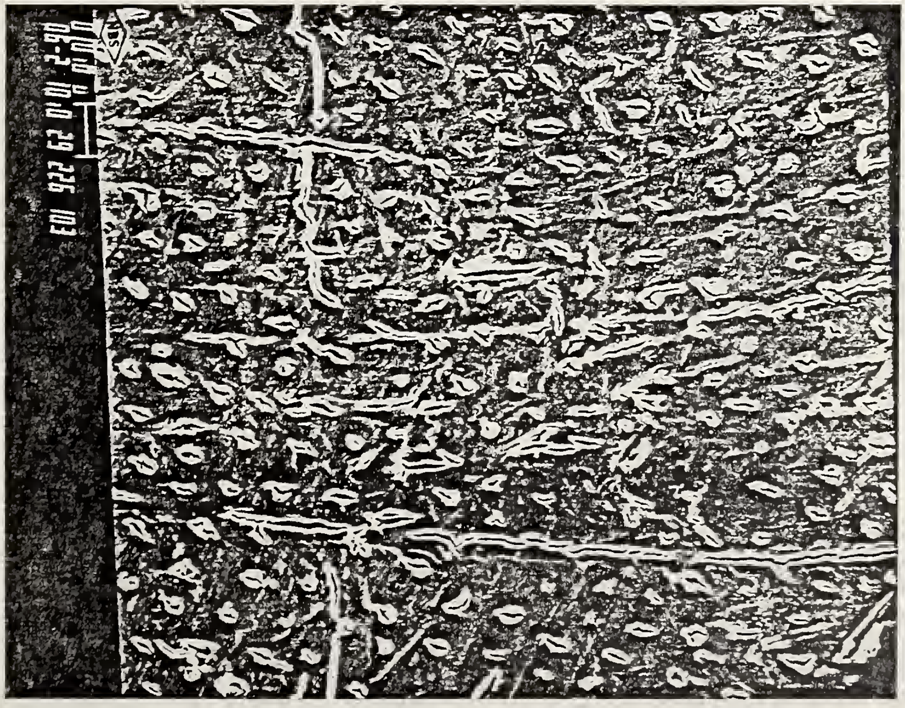

Fig. 9 Dentin. 1 min citric acid then 15% $FeCl_3$ (1 min)

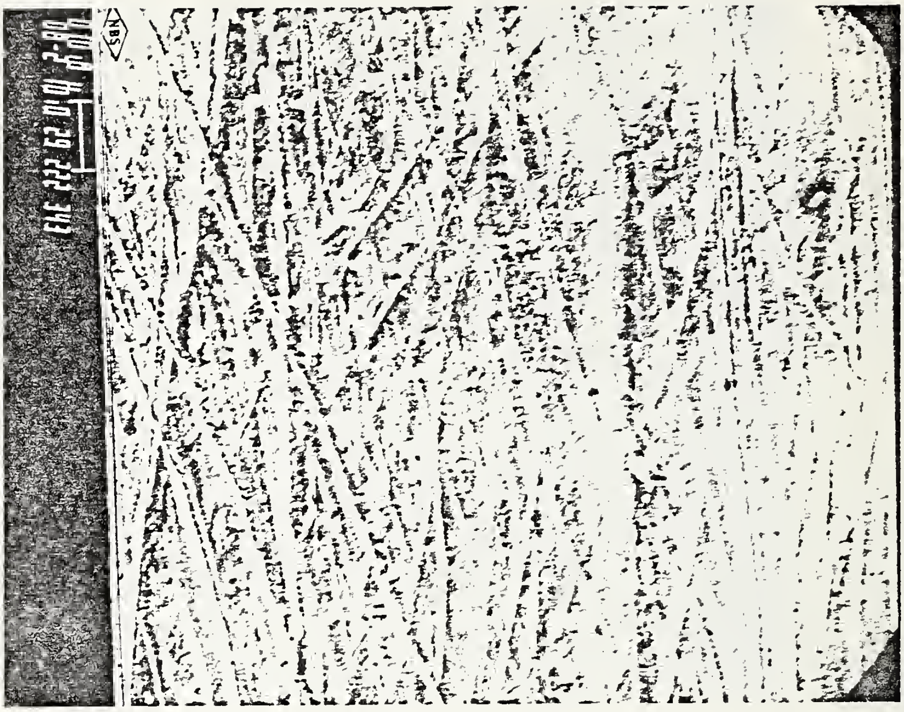

Fig. 10 Dentin. 1M $SnCl_2$ (3 min) - blown off

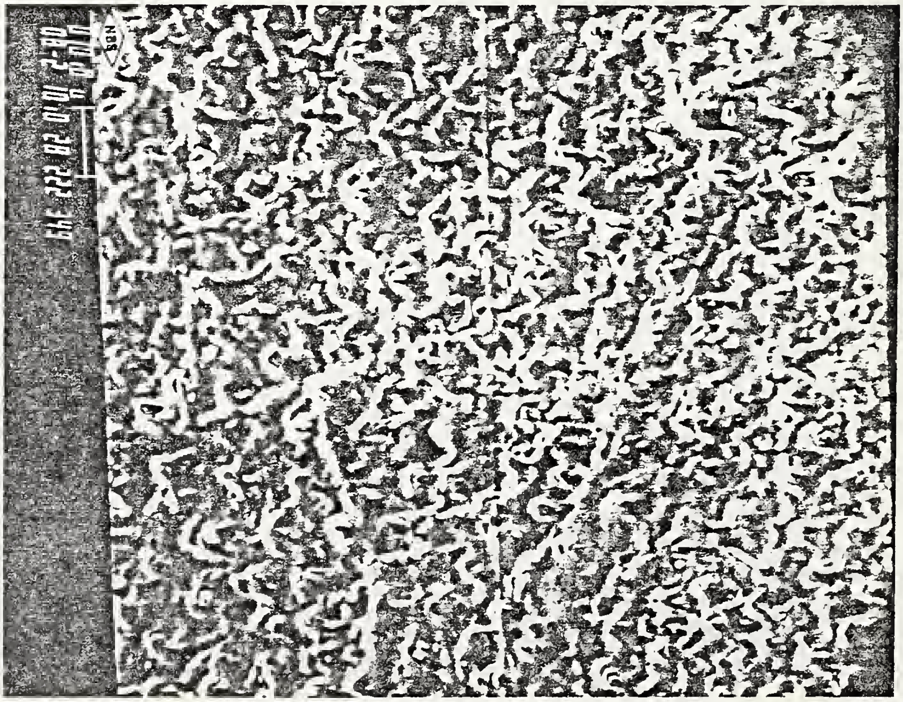

Fig. 11 Dentin. 1 min citric acid. $SnCl_2$ (3 min) blown off

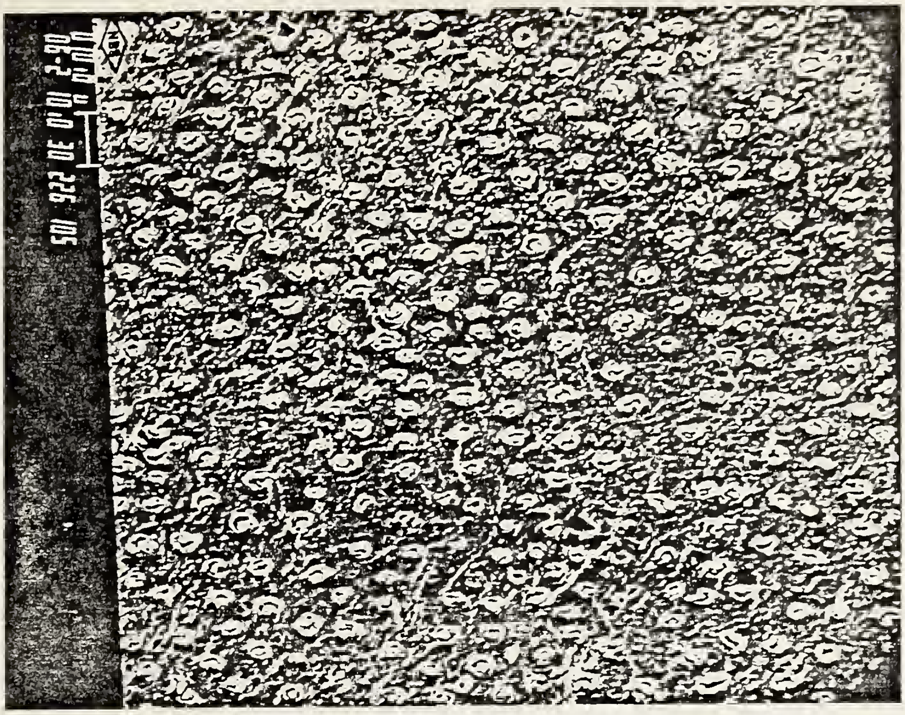

Fig. 12 Dentin. 6.7% ferric oxalate + polyacrylic acid (3 min)

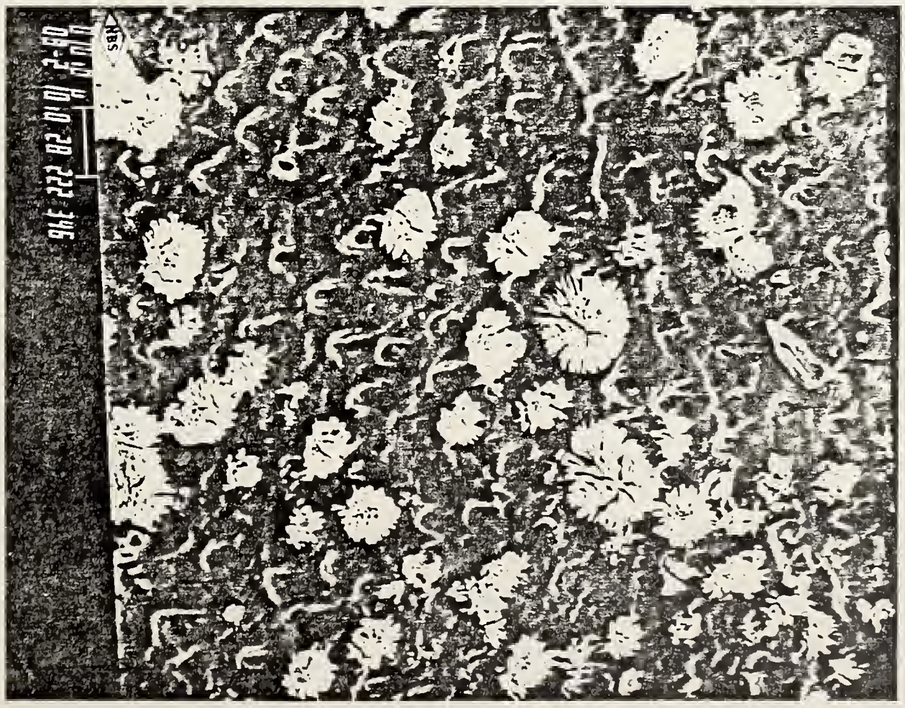

Fig. 13 Dentin. 1 min citric acid then 15% $FeCl_3$ (1 min)

B. Cyanoacrylates

Some cyanoacrylates show a much greater bond strength to dentin than other types of self-curing monomers, after a short period of water immersion. [62,63] This is strongly suggestive of some type of specific interaction, but the nature of this interaction has not been determined.

Most previous workers have examined the effect of varying the ester group of the cyanoacrylate on the bonding to dentin. However, the results of Brauer et al. [63,64] clearly show that the bonding behavior of cyanoacrylates, ostensibly of the same chemical type but from different sources, varies widely. Thus a study of the bonding of the homologous series of alkyl 2-cyanoacrylates is only meaningful when each contains the same amount and type of additives, such as polymerization inhibitors: these additives play a dominant role.

Causton and Johnson [55] have claimed improved adhesion after deposition of mineral layers, together with improved resistance of the bond to water.

An objective of the present work was to investigate the bonding of cyanoacrylates to dentin, with particular reference to the bonding mechanism and ways of improving the strength of the bond and its durability.

The materials examined and some gas chromatographic analyses are indicated in Table 32. All products investigated by gas chromatography were found to consist of one main component, with the exception of Loctite Superbonder 420 which appears to be a 60:40 mix of ethyl and isobutyl 2-cyanoacrylate. All the cyanoacrylates listed in Table 32 were found to have several minor constituents which could not be identified and which differed widely between products.

TABLE 32

Cyanoacrylate Materials

Ester Group	Name	Source	G.C.Retention Times (mm from injection)
βββ trifluoroisopropyl	MBR 4197	3M	32, 122*, 143, 170
Ethyl (60%) + isobutyl (40%)	Superbonder 420	Loctite	32, 125, 132* (60%), 150, 164* (40%), 196
n-Butyl	IS413, medium viscosity	Loctite	130, 141, 146, 172, 177*
Isobutyl	--	Tennessee Eastman	133, 141, 148, 152, 158, 164*
Ethyl	Permabond Type 101	Pearl Chem. Co., Japan	57, 130*, 168

* Major component(s).

The cyanoacrylate was applied to a circular area of enamel or dentin 4 mm in diameter exposed by masking tape. Then an acrylic rod (rod test) or an orthodontic button with a mesh base coated in freshly mixed Adaptic composite (button test) was pressed firmly on to the cyanoacrylate. After 24 hours storage in water the tensile force required to dislodge the rod or button was determined.

The button test was employed because, by application of freshly mixed composite on the cyanoacrylate, it duplicated the potential use of cyanoacrylates as adhesive cavity liners for composite restorations. [65] From Table 33, only Eastman isobutyl and Permabond ethyl gave substantial bond strengths. The bond strength for Permabond was almost double that for Eastman with the button test but they were essentially the same with the rod test. In the rod test (Table 34) it was noted that Permabond polymerized much more quickly than Eastman. Permabond showed a greater spread of results in the rod test with some approaching 11 MPa. The bond strength to Adaptic was measured (Table 33) to allay fears that bond failure was occurring at the interface with Adaptic rather than the tooth surface.

The button test results (Table 33) using human dentin as substrate and citric acid pretreatment were in contrast to those of Brauer [63,64] who used bone-bone interface bonding to investigate adhesion with cyanoacryates. As a result of the strong initial bonding that he achieved, Brauer solicited the cooperation of McInnes and Clayton-Jones of the University of Witwaterstrand, So. Africa to conduct a study of the pulp response induced by pretreatment of unlined labial Class V cavities. While the treatment (0.1 or 1.0% citric acid) removed the dental bur-created smear layer, severe pulpal responses were noted. To circumvent the serious effects of citric

Table 33

Cyanoacrylates: Button Test Results

Material	Substrate	Treatment	No. of Specimens	Mean Bond Strength ± SD (MPa)
MBR 4197, 3M (trifluoroisopropyl)	Dentin	None	5	1.17 ± 0.41
Superbonder 420, Loctite (ethyl + isobutyl	"	"	6	1.27 ± 0.46
IS 413 medium viscosity, Loctite (n-butyl)	"	"	5	2.51 ± 0.9
Eastman (isobutyl)	"	"	6	2.45 ± 0.58
	"	"	6	2.52 ± 1.1
	"	1% citric acid 1 min	6	1.89 ± 0.3
	"	"	6	2.43 ± 0.57
	Enamel	2.5% PolySAM	6	1.4 ± 0.33
	"	None	6	1.18 ± 0.13
	Adaptic	"	6	4.90 ± 1.04
Permabond (ethyl)	Dentin	"	6	4.48 ± 1.29
	"	$CaCl_2$+Na_3PO_4 (3 min)	6	0.54 ± 0.22
	"	"	6	0.77 ± 0.24

Table 34

Cyanoacrylates (rod test)

Material	Substrate	Treatment	No of Specimens	Mean Bond Strength ±SD MPa	Range
Permabond (ethyl)	Dentin	None	6	5.9 ± 3.75	2.68-10.94
Eastman (isobutyl)	"	"	5	6.29 ± 1.25	5.1 - 7.65
			5	5.82 ± 0.92	5.0 - 6.55

acid, the utility of sodium citrate and the disodium salt of ethylene diamine tetracetic acid (Na_2EDTA) has been examined. As will be seen from Table 35, at least for the bone substrate, the 1% sodium citrate or 1% Na_2EDTA pretreatment do not lower the bond strength of the bone to bone joints (bonded with isobutyl 2-cyanoacrylate) that had been stored in water for 24 hours or thermocycled for this length of time between water baths at 5°C and 55°C. However, a pretreatment using 17% Na_2EDTA solution which is an excellent medium to remove the smear layer reduced the strength of the bond. Similar results were observed in pretreatments with Dical, a calcium hydroxide based material. Since very satisfactory bone-bone adhesion for time periods useful for temporary cementation were obtained with sodium citrate or Na_2EDTA it would be desirable to encourage a cooperative study of the effect on the underlying pulp of using them in pretreatment of exposed dentin surfaces.

No direct proof of covalent bonding between protein and cyanoacrylate via initiation of cyanoacrylate polymerization by the basic groups in protein, has been published. Leonard _et al_ [66] have shown that amino acids in aqueous solution will attach as end groups on polycyanoacrylate chains. This, in conjunction with the obvious ability of cyanoacrylate to bond to skin and other proteinaceous surfaces, has resulted in the assumption that covalent bonding to protein occurs. One technique for examining the mechanism of bonding is infrared spectroscopy (IR).

Fourier Transform IR spectra (Nicolet FT-IR) of dentin and Permabond cyanoacrylate were subtracted from the spectrum of a mixture of both. The IR spectra of dentin, steerhide collagen and mixtures of Permabond with dentin and with steerhide collagen after extraction of cyanoacrylate with dimethyl formamide were recorded. FT IR showed no evidence for new bond

Table 35

Effect of Pretreatment of Bone on Tensile Strength of Bone Joined with Cyanoacrylate Adhesive

Treatment	Tensile Strength of Bond	
	Stored 24 hr in 37° water MPa	Thermocycled 24 hr 5-55°C water MPa
Control	4.8 ± 0.5	3.3 ± 0.8
1% citric acid in 30% EtOH	6.3 ± 0.5	4.0 ± 0.3
1% Na citrate in 30% EtOH	5.8 ± 0.6	4.4 ± 0.8
17% Na_2EDTA Aq. Sol.	2.6 ± 0.6	- - -
1% Na_2EDTA in 30% EtOH	4.7 ± 0.4	5.1 ± 1.5

formation as a result of any chemical reaction which may occur between cyanoacrylate and dentinal protein. Likewise, no residual cyanoacrylate could be detected in the IR spectrum of dentin-cyanaoacrylate or steerhide collagen-cyanoacrylate mixtures after washing with excess dimethyl formamide. Further, a mixture of Permabond with basically dry steerhide collagen did not initiate polymerisation after 15 min. In contact with a moist powder Permabond will polymerise in less than 20 sec. The use of dry collagen eliminates competition of water with the basic groups in the protein for reaction with cyanoacrylate; dry collagen should promote the reaction of cyanoacrylate with collagen. If cyanoacrylate will not react with pure collagen, the chances of chemical reaction with the tightly coiled cross-linked collagen embedded in hydroxyapatite in the presence of large amounts of water, proteinaceous fluid and dentin debris, appears remote. Amino acids with amine or hydroxyl side groups are a minor proportion of the protein chain and are frequently involved in inter or intra molecular hydrogen bonding. In contrast, the great amount of water present in physiological systems may overwhelm other potential initiators.

The decrease in bond strength of cyanoacrylates to dentinal surfaces on exposure to moisture has been attributed to degradation of the polymer. However, the decrease in bond strength appears much too rapid to arise from degradation. If primary bonds, covalent or ionic, are not formed, then penetration of water along the bond interface would rapidly break down secondary bonds. Self curing methacrylates will bond well to enamel etched with 2% phosphoric acid by secondary bonds but without tag formation. [67] Such bonds resist water penetration until stressed, when rapid failure occurs. [68]

Why do cyanoacrylates adhere better to dentin than other self curing resins? The answer probably is in the unique characteristics of cyanoacrylates: they polymerize rapidly by initiation at the tooth surface (good adaptation, intimate contact); polymerize only in thin films (minimal polymerization stresses) and are very polar polymers (hydrogen bonding and dipole interaction with protein). It is certainly reasonable to expect that crystal growth on the dentin surface will improve bonding by mechanical interlocking. Treatment of dentin with the calcium phosphate *in situ* precipitation technique virtually eliminated bonding (Table 33). This technique will deposit amorphous calcium phosphate rather than crystals. The decrease is presumably caused by covering the protein with such a mineral layer.

Finally, if adhesion of cyanoacrylate to dentin is by secondary bonds only, then the breakdown of the bond in water will not be affected by improving the resistance of the polymer to degradation.

C. "Reactive Adhesive" Formulations

A series of "reactive adhesives" were formulated and their bond strength to bone was determined. These reactive adhesives were formulated with various components to produce a chemical cure within a few minutes. The adhesives are usually prepared by dissolving an elastomer in a monomer or oligomer solution. Polymerization takes place through a free radical mechanism. The cured system is toughened by the elastomeric domains which are incorporated into the structure by grafting.

Adhesive formulations were prepared from elastomers that were soluble in the monomers used (acrylic or methacrylic acid and methacrylate ester monomers) benzoyl peroxide initiators and inhibitor (butylated hydroxytoluene, BHT). The second component was a solution of a tertiary amine accelerator with which the substrate surfaces (bone) are treated prior to application of the elastomer-monomer component. The bond strength of the joint between two pieces of bone substrate was evaluated after storage in water.

A commercial polyurethane (Estane 5712), reported to be a reaction product of tetramethyleneglycol ethers of varying molecular weight and methylene diisocyanate was found to be soluble in the monomers we were using. Joints prepared from a reactive adhesive formulation composed of 33% Estane, 33% decamethylene glycol dimethacrylate (DMDMA), 17% acrylic acid, 17% methyl methacrylate, 0.04% BHT and 3.6% benzoyl peroxide in which the substrate had been treated with 10% alcoholic dimethyl-p-toluidine did not debond on extended storage in water. The highest bond strength following storage of the test specimens in water for 3 months was about 1 MPa which is much lower than the strength that can be attained with alkyl 2-cyanoacrylates.

Replacement of methacrylic acid for acrylic acid decreased adhesion to bone. Substitution of methacrylate esters such as 2-ethylhexyl acrylate for acrylic acid resulted in mixtures in which the polyurethane was insoluble. The rubbery component did not dissolve completely on using 1,10-decamethylene glycol dimethacrylate. Formulations with Estane 5713 and 5740 were also employed, but the elastomeric component did not dissolve in the monomer system. Compositions containing other rubbery toughening agents such as vinyl terminated butadiene-acrylonitrile (reactive liquid polymer Type 1300 X-22 and 1300 X-23) or chlorosulfonated polyethylene (Hypalon H-30) did not yield satisfactory adhesives. Pretreatment of the bone with 1% citric acid or 1% sodium citrate did not improve bonding. Thus, the reactive adhesives investigated did not look very promising for bonding mineralized tissues and their study was discontinued.

III. Wear Resistance and Mechanical Properties of Dental Composite Restorative Materials

In connection with our overall effort in developing improved composite restoratives the objective here is to develop, or make use of, appropriate techniques to measure wear resistance and mechanical properties of dental materials and to use the forthcoming data as performance indicators to predict *in vivo* durability of these materials. The completion of the development of these methods to a satisfactory state is particularly important because of the long times and efforts required for clinical evaluations. In order to accomplish this task, some fundamental research on wear and related mechanical properties is being done to obtain a better understanding of the relevant mechanical and chemical degradation processes. This information will be of use in determining the principal variables of influence from which appropriate modifications may be incorporated in the wear apparatus to obtain meaningful results. In addition, the improved understanding of ways in which specific mechanical properties of composite systems correlate with wear behavior is expected to be instrumental in developing more durable systems.

Two types of wear tests have been, or are being, developed here which comprise a classical pin and disc apparatus and an erosion technique. Although these particular methods are not necessarily expected to be used as final performance indicators, they do give basic information relevant and possibly essential to the development of an appropriate durability test, as will be apparent in later sections of this report. Complementary efforts involve microdefect analysis using x-ray and optical microscopic observation of damaged regions made resolute by a silver staining technique. In order to obtain a relevant wear test, we assert that the subsurface damage resulting from *in vitro* wear should resemble that obtained from *in vivo* worn specimens.

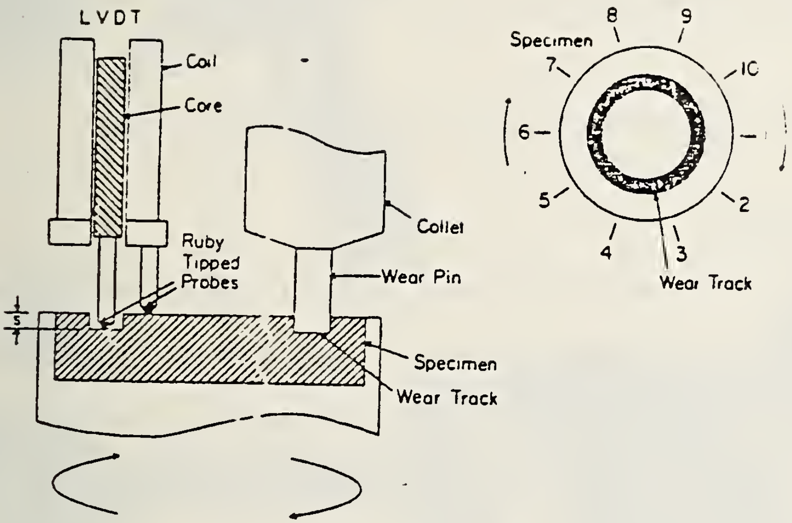

Fig. 14. Schematic illustration of principle of pin and disc measurement.

Other aspects examined in these studies are the couplings between chemical solvents and wear and between subsurface damage generated during wear and wear itself.

The following discussions include the work performed during this fiscal year on wear and mechanical properties of dental composites and their component materials.

A. Pin and Disc Wear and Related Knoop Hardness Number (KHN) Measurements

1. Instrumentation

The pin and disc wear apparatus is completely automated comprising three identical rotating platforms containing the disc shaped specimens of the material to be investigated. The principle of operation is depicted by Fig. 14. A stationary slider (pin) of human enamel, or appropriate substitute, impinges on each of the rotating specimens producing a wear track of 12 mm mean diameter. The slider is loaded with weights to obtain the desired normal stress which is usually 10 MPa. The depth of the wear track is measured periodically at 10 equally spaced positions along the track circumference using linear variable differential transformers with ruby tipped probes as shown in the figure. Distilled water at 37°C flows over the specimens to control temperature, lubricate, and wash away debris. Figure 15 is a close-up photograph showing the specimen and cup, wear pin and mounting collet, probes and transformer, and the thermocouple junction.

A portion of activity during this period was dedicated to instrumentation maintenance. Some of the maintenance was deemed necessary by a gradual increase in unreliability which was eventually traced to a power supply instability in the microcomputer controller. Eventually the computer became inoperative. The power supply failed completely and inflicted damage on

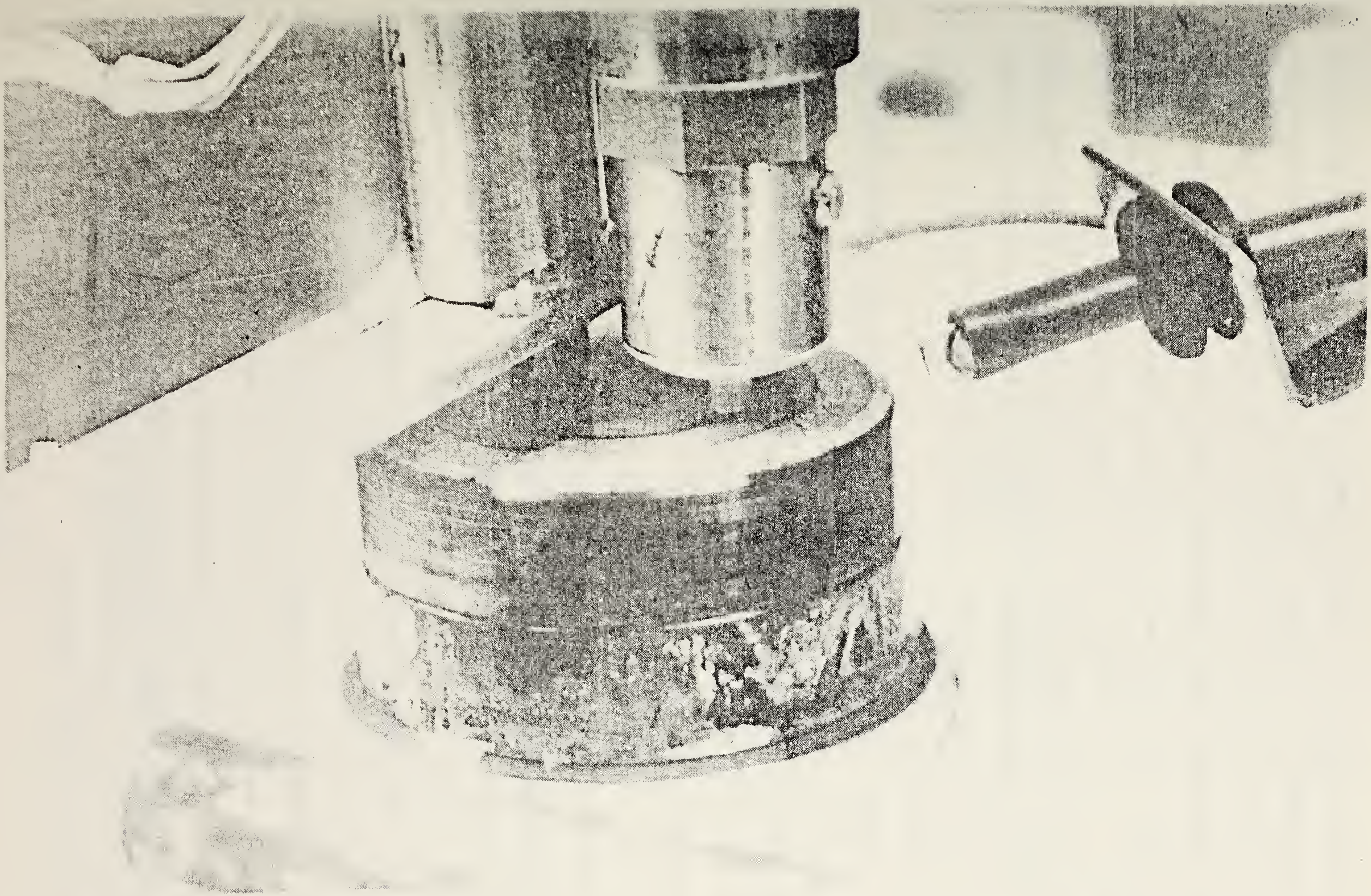

Fig. 15. Close-up photograph showing wear pin and mounting assembly, transformer assembly, and water jet nozzle.

some other components. After the computer was repaired and returned to us, its performance was excellent, but only for several weeks after which the power supply failed for the second time. In order to complete the set of wear measurements being undertaken at that time, an external power supply was connceted. After these were completed the computer was again returned for repair. It is our opinion that the present version of the computer's power supply has insufficient capacity for its application. Unfortunately, space limitations make it difficult to install a larger one. A separate external power supply may be the answer. We have informed the manufacturer that this is a problem they will have to solve.

Periodically, about once a year, it is appropriate to re-evaluate the experimental imprecision and LVDT (linear variable differential transformer) and related electronic drift rate. This is accomplished by simulating a wear run using polished brass discs as specimens. Since the wear pins are always maintained at a distance from the specimens, no wear is generated. Ideally, the apparent track depth would be zero at all times. In Fig. 16 the apparent track depths are plotted against time for the No. 1 position (out of 10 possible ones around the wear track circumference). Since the drift rates are not known during actual wear runs, the standard deviation values included in the figure apply to the residuals about the average in lieu of those about the statistically fitted straight lines shown. For a wear rate of 1 μm/hr a drift rate of 15 Nm/hr will produce an error of 1.5%. This error is small in comparison to that caused by specimen to specimen variation of composites or that attributed to inhomogeneity within a composite specimen. In some cases, the standard deviation of the residuals about statistically fitted straight lines on actual wear data are often less than those given in Fig. 16. The lower variances result from the drift rates being unknown for an actual wear run.

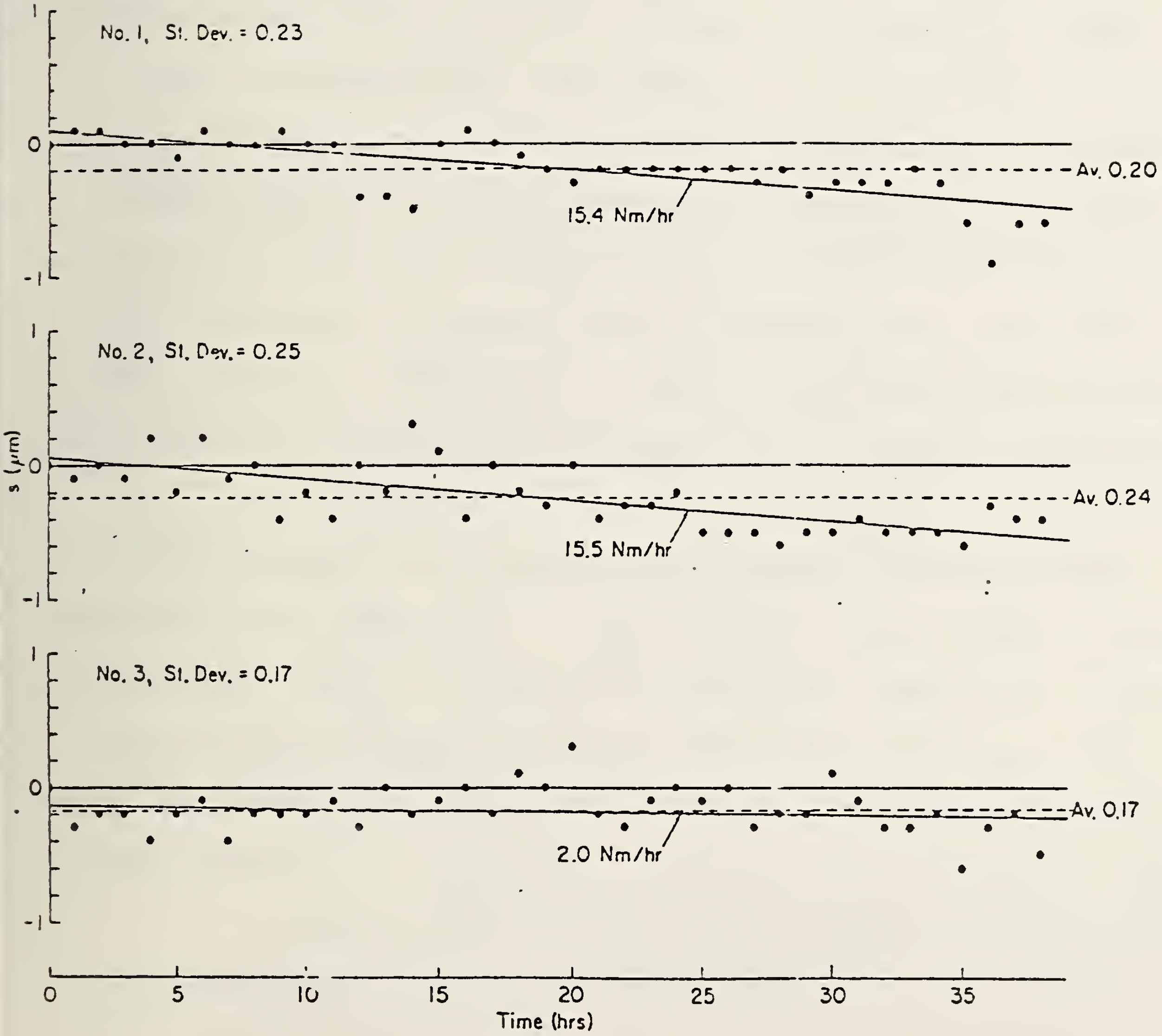

Figure16. Apparent track depth s versus time for a "no-wear" run. The drift rates shown are obtained from linear regressions on the data.

During this reporting period, some improvements were made on the method of calibrating the track depth measurement system. A calibration procedure is conducted periodically about every three months. In this process, 1 μm of differential displacement is made to produce 10 mV DC differential from the LVDT conditioning amplifier. The LVDT core displacement is determined by using a step shim comprising five 150 μm glass shims glued together as shown schematically by the inset at the top of Fig. 17. During calibration the core probe rests against position 0 which extends over the entire length of the shim as revealed by the inset. The other probe, which is attached to the LVDT housing, rests against any one of the other four positions. The thickness of the shim at each position is measured by a micrometer. Although the micrometer is read to 1 μm, readings are not expected to be better than ±2.5 μm.

The results from the most recent calibration are included in Fig. 17. The LVDT readout in terms of displacement is plotted against the shim height relative to the number 0 position. The straight line shown is obtained from a linear regression on these data. The position numbers indicated at the data points correspond to the positions shown in the inset at the top of the figure. Departures from linearity and unity slope are not visible on this plot for the data obtained at each of the three wear stations.

Figure 18 gives the residuals about the straight lines plotted against shim height for the three wear stations. In this plot distinctions between the three sets of data and apparent departures from linearity are clearly visible. The LVDT outputs are read to 1 mv which corresponds to an ordinate value of 0.1 μm on the figure. It is clear that the data are not entirely randomly distributed. The fact that the data tend to aggregate at each position indicates the existence of systematic error in the shim thickness

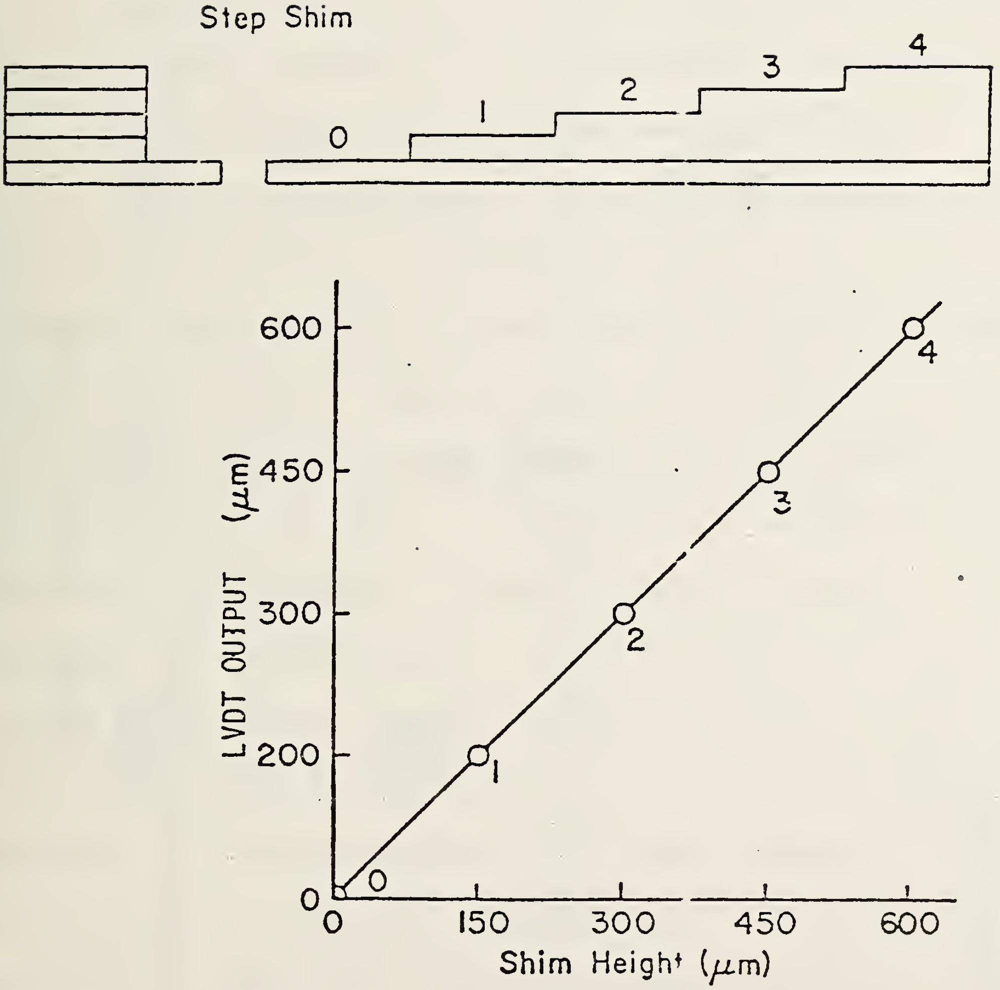

Figure 17. Illustration of calibration procedure. For explanation, see text.

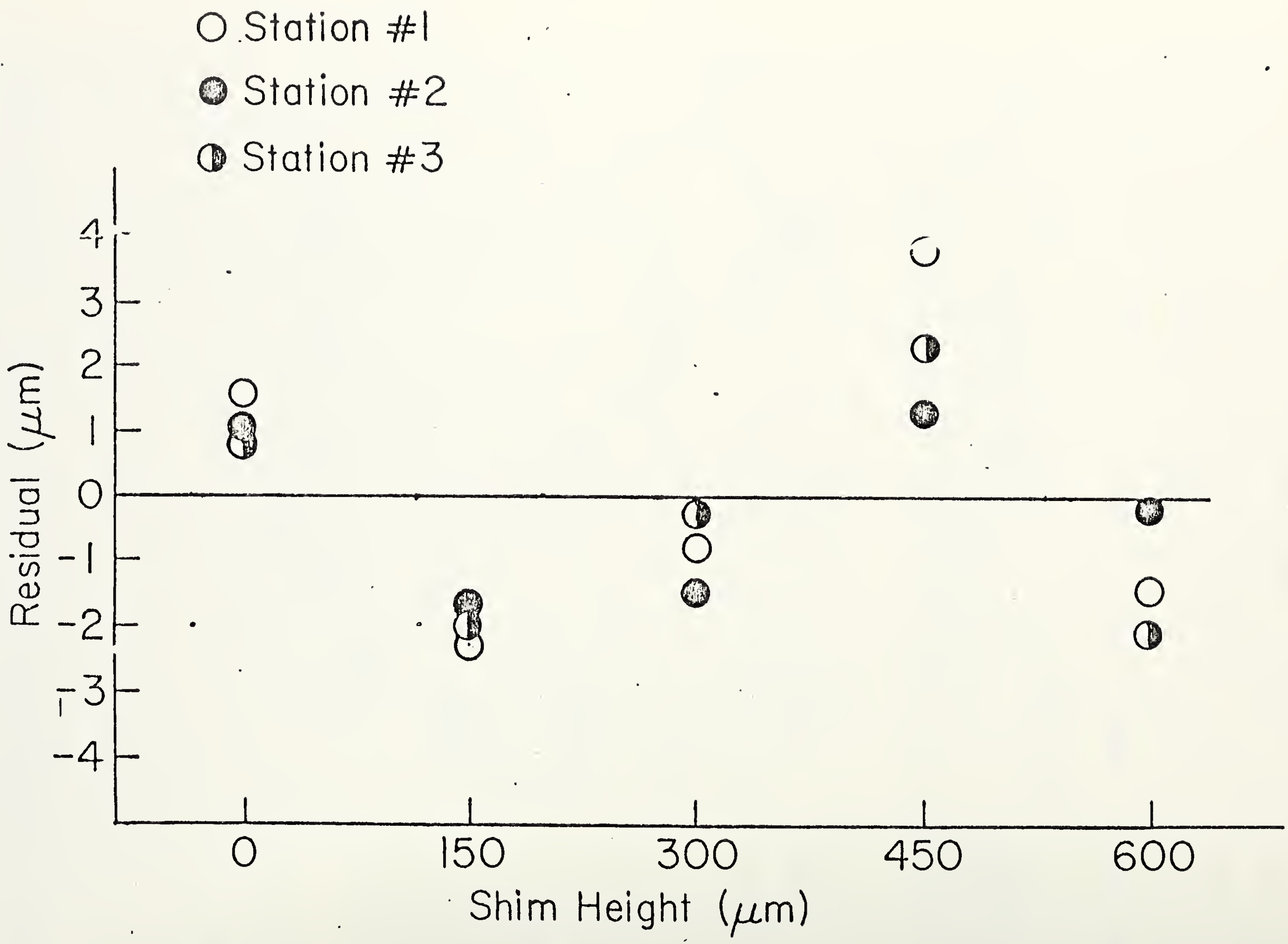

Fig. 18 Displacement residuals about the fitted straight line shown on Fig. 17 for the three wear stations.

measurement. These are attributed to nonlinearity (screw displacement versus rotation) of the micrometer. The errors shown are commensurate with those expected from nonlinear micrometer response.

The track depth measurement system is calibrated over 600 μm. The largest track depth measured so far on a wear specimen is 150 μm.

A manuscript which includes descriptions of the wear instrumentation and the calibration procedure has been submitted for publication [69].

2. Influence of Silanization Treatment on Wear

Research by Brauer and Chen* of our Group has pointed to the possibility of catalyzing the silanization treatment of glass filler particles with an amine as a means of improving the silane coupling action between filler and resin matrix. Improvement in this bonding would presumably be reflected in wear resistance. The specimens were prepared with the compositions given in Table 36. The 1.9% silane catalyst concentration produced the highest value in diametrical tensile strength. Although wear measurements were attempted, the results were unsatisfactory. The principal difficulty was that the wear specimens were not sufficiently homogeneous to obtain meaningful data. Considerable improvement is anticipated if times for equivalent cures are extended. This investigation was interrupted by Dr. Brauer's recent illness. As a result of recent termination of Chen's visit to NBS, it is not clear at this time when this activity will be resumed.

3. Mechanically Induced Damage and Wear on Composite Restoratives

In the FY80 Annual Report [4], we included some preliminary data on the wear of Adaptic at various normal stress levels ranging between 2.5 and 20 MPa. In most cases the data reveal abrupt changes in the wear rate by roughly a factor of two during the course of wear as depicted

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*Guest Worker, Food and Drug Administration

TABLE 36

Composite Composition Used to Study Influence of Silanization Catalyst on Wear and Mechnical Properties

Ingredient	Composition %		
Powder	#1	#2	#3
Corning Glass #7724	98.5	98.0	96.6
A-174 Silane ≡ 3-methacryloxypropyl-trimethoxysilane	0.5	0.5	0.5
Benzoyl peroxide	1.0	1.0	1.0
η-propyl amine (silanization catalyst)	0	0.5	1.9
Liquid			
BIS-GMA	72.1		
1,6-Hexamethylene glycol dimethacrylate	27.5		
Dimethyl-p-toluidine	0.23		
Butylated hydroxytoluene (inhibitor)	0.2		

Powder-Liquid Ratio = 3:1

symbolically by Figure 19. The occurrence of these breaks (at the onset of B) is usually earlier with increasing stress. This phenomena is interpreted as the initial wear (in region A) being dominated by an adhesion and/or abrasion process. As wear progresses subsurface damage increases to a point where severe breakdown occurs from fatigue. At this point a steady state is obtained for which wear is enhanced through the addition of a fatigue mode (Region B). The occurrence of the onset of B at earlier times with increasing stress results from more extensive damage generated at the larger stresses.

This behavior is more general in that it is not restricted to composite restoratives. Similar results were obtained by Prof. Dowson and coworkers [70] at the University of Leeds on ultra high molecular weight polyethylene (UHMWPE). The principal distinction between their techniques and ours is that their disc is the abrader, and their pin is the specimen. Their configuration, accordingly, leads to a constant normal stress on the specimen, whereas our produces an oscillating stress with periods corresponding to revolutions.

The results of their research on UHMWPE are in many ways similar to our on Adaptic. In their work the wear rates in regions A and B differ by about a factor of two, and the time for the onset of B decreases with increasing stress. The principal difference is in the time required for the onset of B. In our work these times range between 5 and 20 hours, whereas theirs, 100 to 600 hours. Their stress range, 3.5 to 22 MPa, is similar to ours (2.5 to 20 MPa). Whether this distinction in times for the onset of B may be attributed to the differences between techniques or material difference (UHMWPE vs Adaptic) is not clear at this time. Intuitively, cycling stress is expected to produce failure at an earlier time, which is evident from comparison of their and our results.

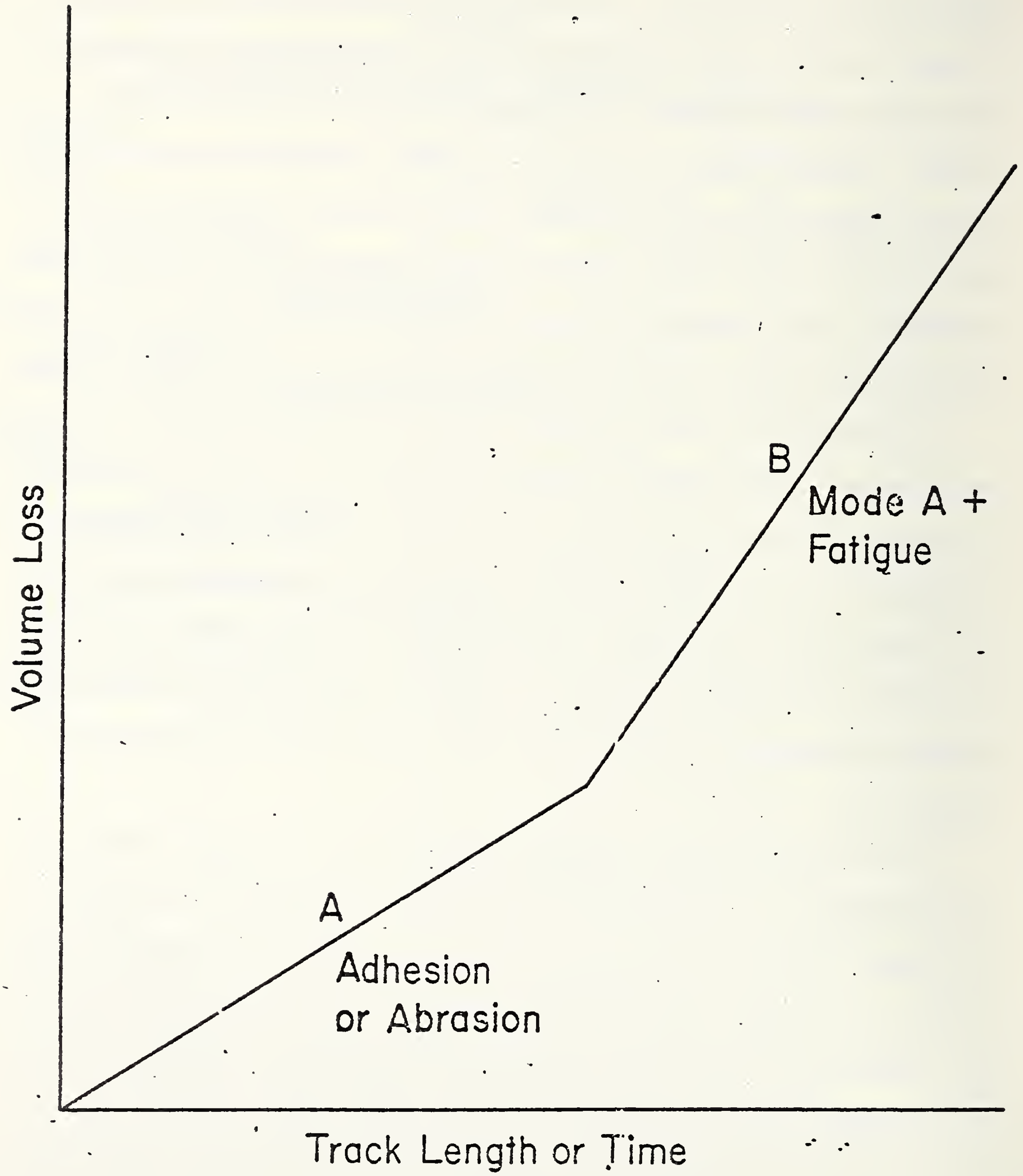


Fig. 19. Symbolic wear response resulting from damage generated during wear.

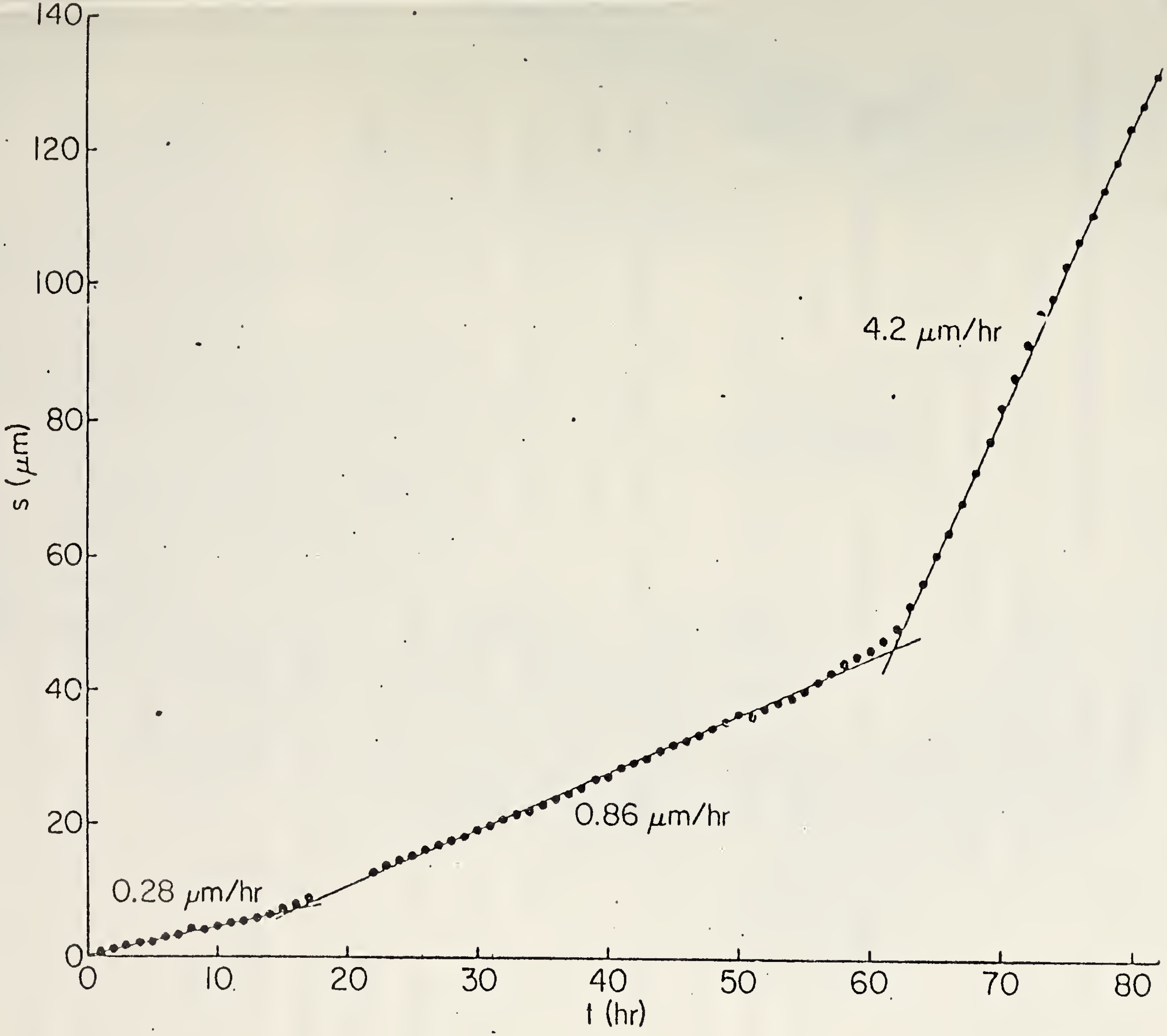


Figure 20. Extended wear on *Adaptic* showing track depth s versus time t.

The silver staining microdefect analysis [71] was used on specimens on which wear was terminated intermediately in both regions A and B. The specimen with wear terminated in A showed essentially no subsurface damage, whereas the one in B revealed considerable damage similar to that observed on occlusal surfaces of _in vivo_ worn specimens. Since this analysis is destructive, we were not able to obtain damage assessments as wear progresses.

Very recently we obtained some results on Adaptic using a stainless steel pin at 10 MPa for 80 hours, which is a longer time than any used previously by us. The results are shown on Figure 20, where the wear track depth is plotted against time. In addition to the aforementioned break at about 15 hours, a larger change occurs at 60 hours, where the wear becomes essentially catastrophic, being nearly ten times as great as the initial value.

A plausible interpretation for the second break is revealed by the silver staining micro-defect analysis for which the results are displayed on Fig. 21. From the micrograph a fault line is apparent which emerges downward from the corner of the wear track and eventually turns parallel to the wear surface at a depth of about 300 μm. The fault line demarcates a damaged layer which extends to the surface and wears at the high rate displayed on the right hand side of Fig. 20.

A somewhat general observation in clinical tests on composites is that anatomic form deterioration seems to accelerate with time (see, for example, Ref. [72]). The increasing wear rate resulting from wear mode conversion, or addition, and severe subsurface damage may provide partial explanations for this phenomenon.

A manuscript including the results of this activity has been submitted for publication [73].

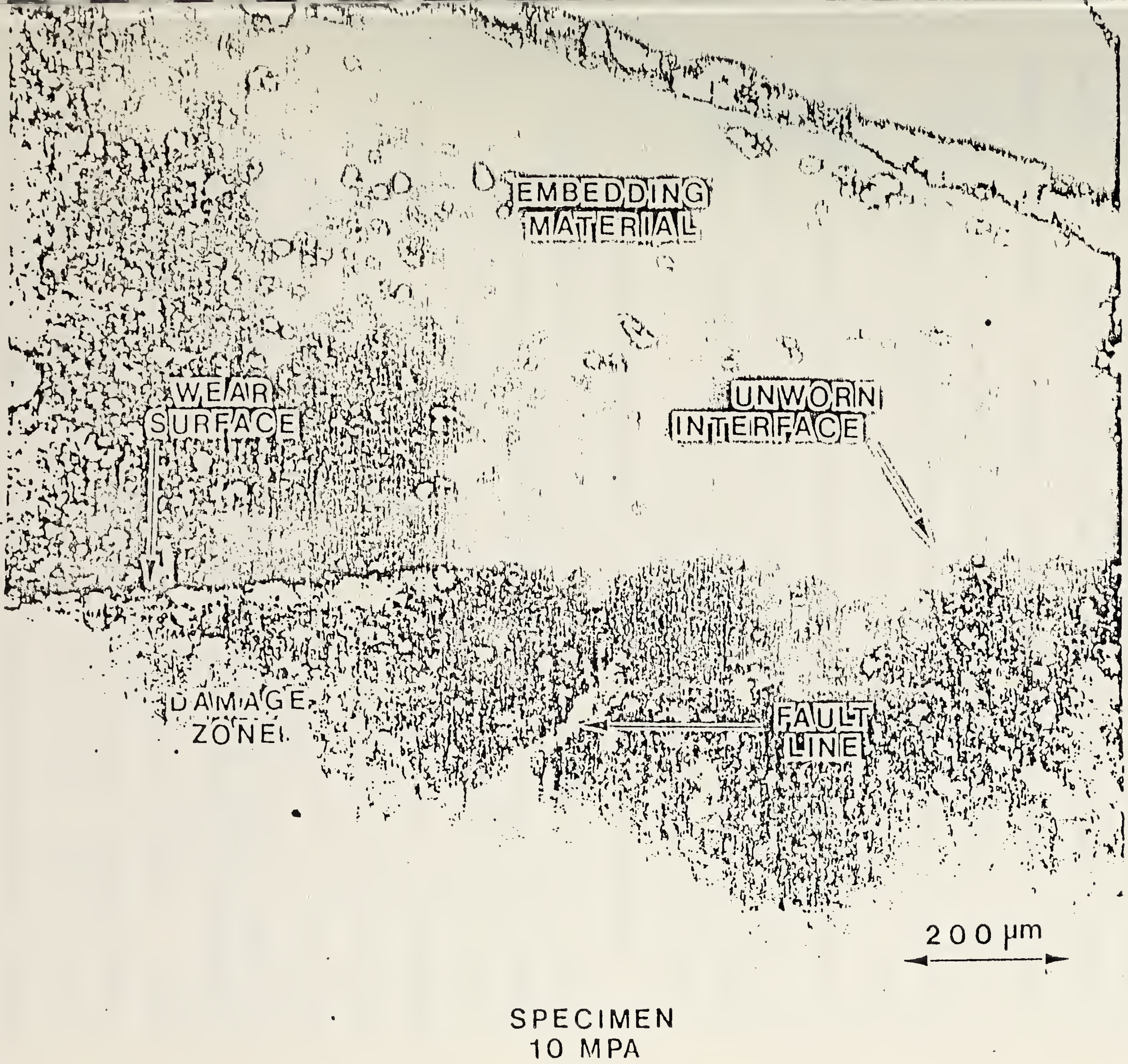


Fig. 21. Micrograph showing worn and unworn surfaces of an Adaptic specimen over 83 hours wear at 10 MPa stress.

4. Chemical Softening of Dental Composites

Another process which may cause deterioration in dental composites is the interaction with chemical solvents. The solvents selected are among those recommended in Reference [4] for food simulation. These solvents are water, ethanol-water solutions, acetic acid, and heptane. The greatest interactive effects are expected when the solvent has a solubility parameter value which approximates that of the polymer base, which usually comprises BIS-GMA. Preliminary tests involved immersing specimens of Adaptic in ethanol, cyclohexanone, and distilled water at 37 °C for two weeks. Immediately afterwards pin and disc measurements using stainless steel pins were made. Cyclohexanone was selected before we were aware of the FDA Report [4] recommending food simulators to be used in connection with the evaluation of food container lining materials.

The results are shown on Figure 22, where the wear track depth at 10 MPa is plotted against number of cycles or disc revolutions. Ethanol produces the largest effect for which 11 microns are removed in the first cycle. With water a slight decrease is observed, which may be attributed to roughening of the initially polished surface. Subsequent measurements with data taken every hour (about 1500 rev/h) are depicted by Figure 23. Over the first hour the wear of the chemically-soaked specimens is severe in contrast to that for the water-soaked one which is negative, presumably because of the "break in" process mentioned above. Through the remaining 44 hours, the wear of the chemically soaked specimens exceeded that for the water soaked one by about a factor of three. The total wear did not exceed the depth of the damaged region which is about 200 μm as revealed by the silver staining technique.

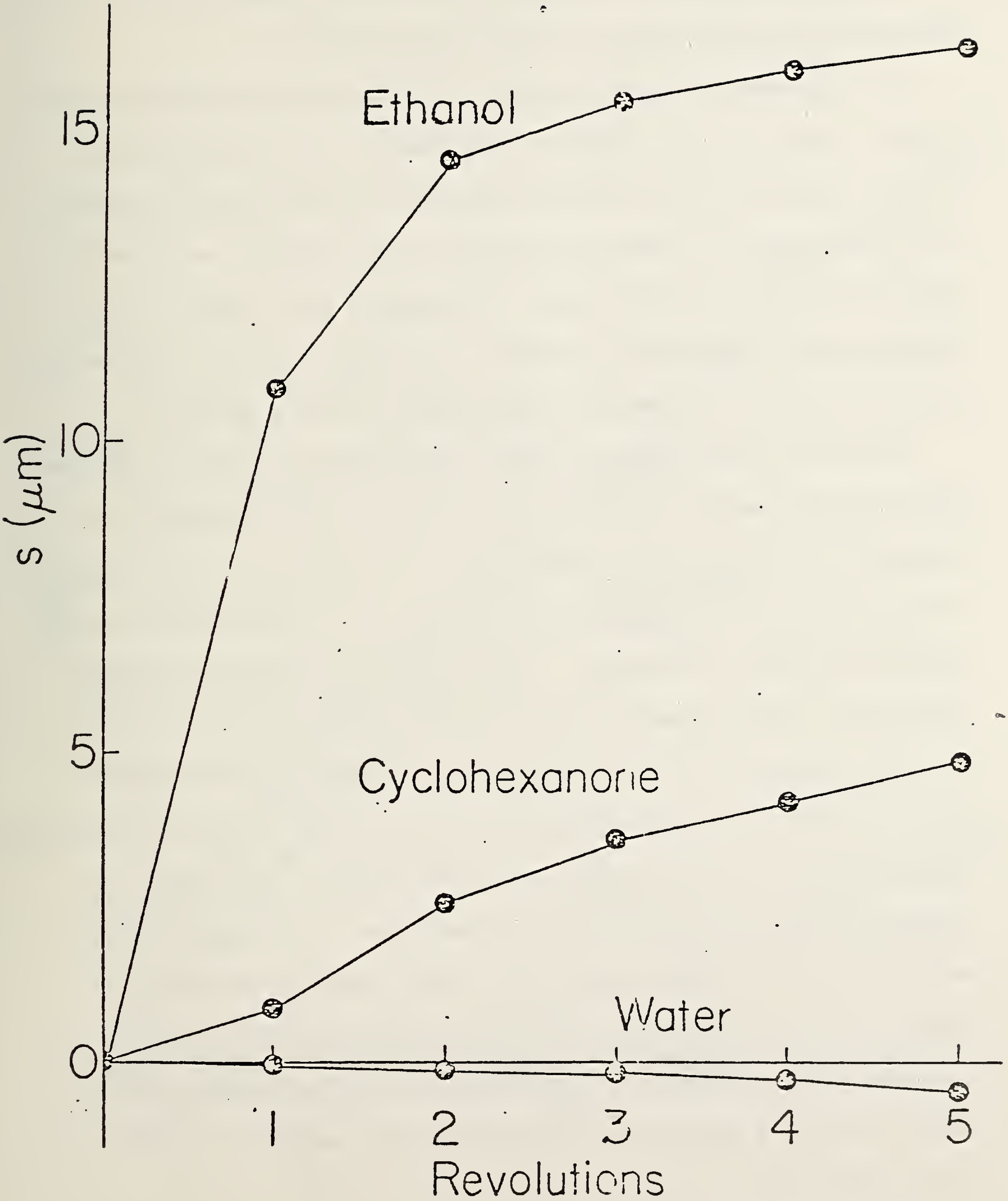


Figure 22. Track depth s over first five revolutions for Adaptic specimens soaked previously in ethanol, cyclohexanone, and water.

The resulting loss of hardness of the dental composite due to various chemicals has been reported in a previous report [4].

All the chemical solvents used in the work mentioned previously are in their pure form. One question which remains to be studied is the effect of concentration of various chemicals on the degree of softening of BIS-GMA polymer. Chemicals existing in the intraoral environment are believed to be diluted with water. Therefore a set of tests using ethanol/water mixtures was conducted; the change in surface hardness and in wear resistance of chemical soaked composites were measured.

Unfilled BIS-GMA polymer samples were immersed in 100, 75, 50, and 25% V/V ethanol/water solution and the drop in surface hardness was monitored as a function of immersion time. The data are shown in Figure 24. A severe decrease in hardness was observed in all these immersed samples especially that in 75% ethanol. By locating the solubility parameter components of these chemicals used so far in the softening study on a δ_a vs δ_d (association and dispersion part of the solubility parameter) plot (Fig. 25), it becomes apparent that BIS-GMA has a solubility parameter with $7 \leqq \delta_d \leqq 9$ and $2 \leqq \delta_a \leqq 16$. The wide spread of the value of δ_a component of BIS-GMA molecule is believed to be a consequence of the monomer size of BIS-GMA. According to the Hildebrand theory [75] for mixed solvents, any mixture of chemicals with solubility parameters in the range mentioned above will be a good solvent for BIS-GMA. Such a result was indeed observed in our recent work on methanol and DMSO mixture (Fig. 26).

Immediately after soaking Adaptic specimens in 25, 50, and 75% solutions of ethanol in water, pin and disc measurements were made on these three specimens. The results including those using the 0 and 100% ethanol solutions from previous work are shown in Fig. 26. The wear track

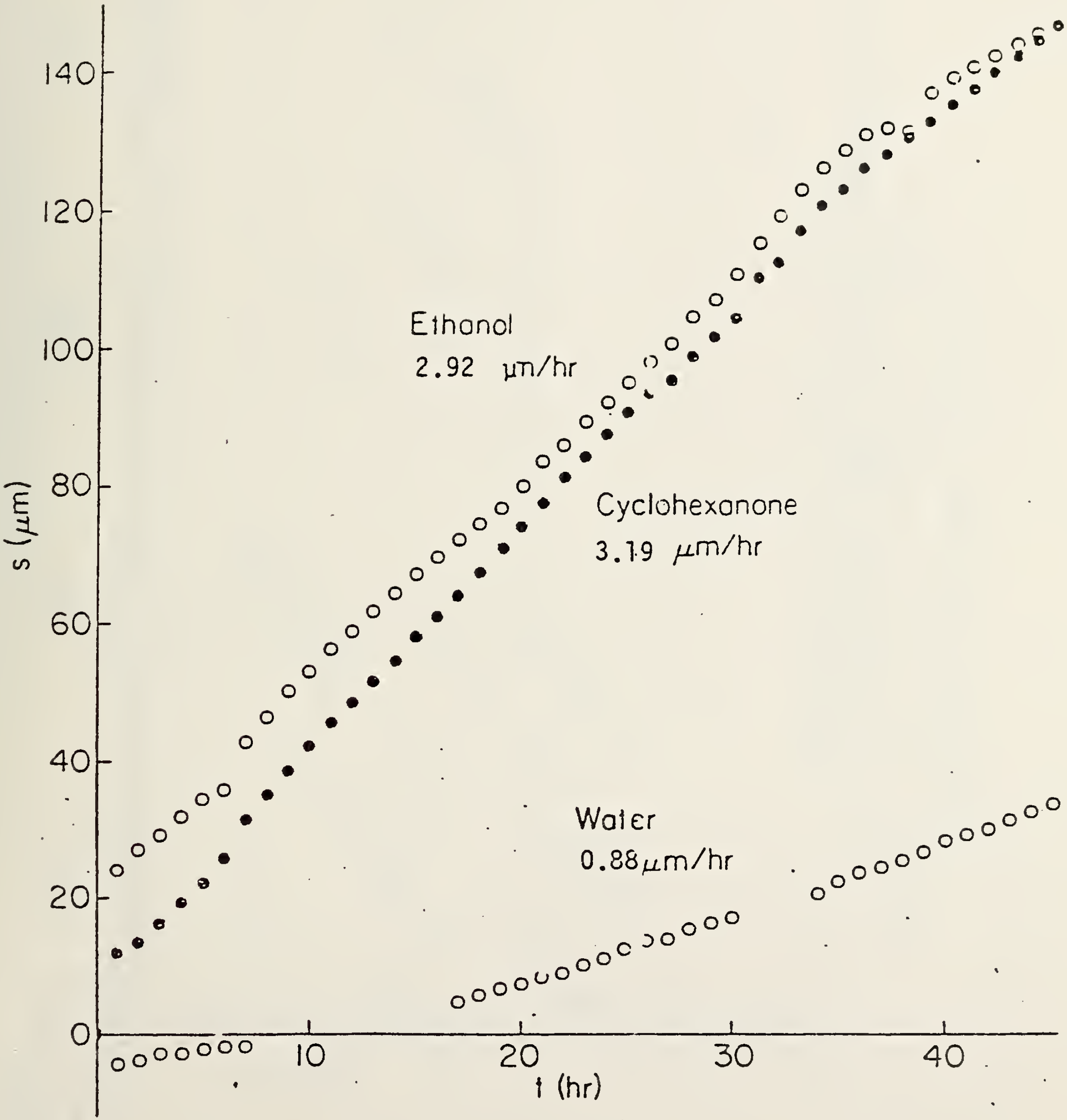


Figure 23. Extended wear for specimens used in Figure 3. Track depth s is plotted against time. (1 hr = 1500 revolutions)

Figure 24. Effects of various concentrations of ethanol in water on Knoop Hardness Number of unfilled BIS-GMA resin samples (30% wt TEGDMA)

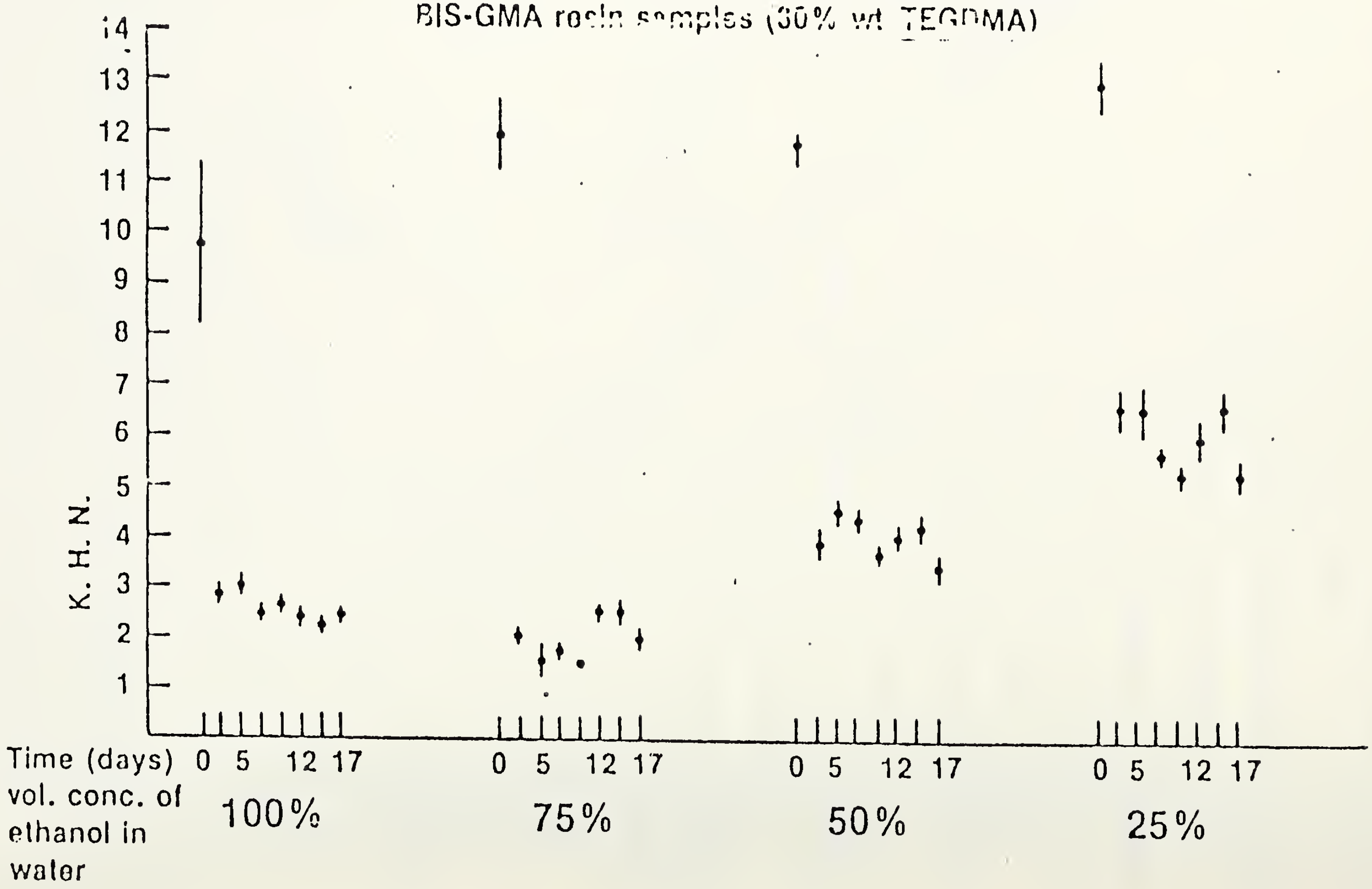
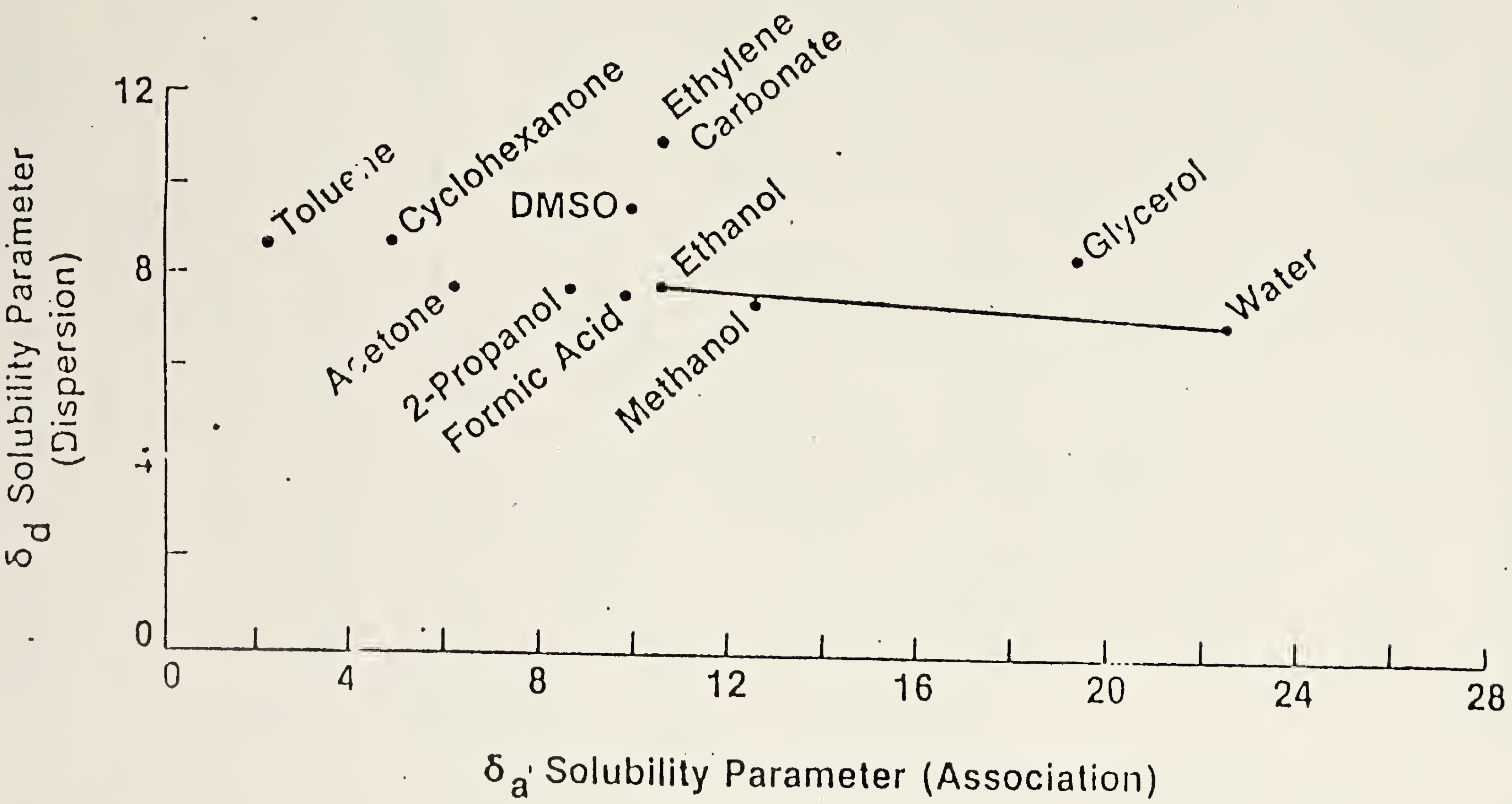


Figure 25. Solubility Parameters of Various Solvents and BISGMA



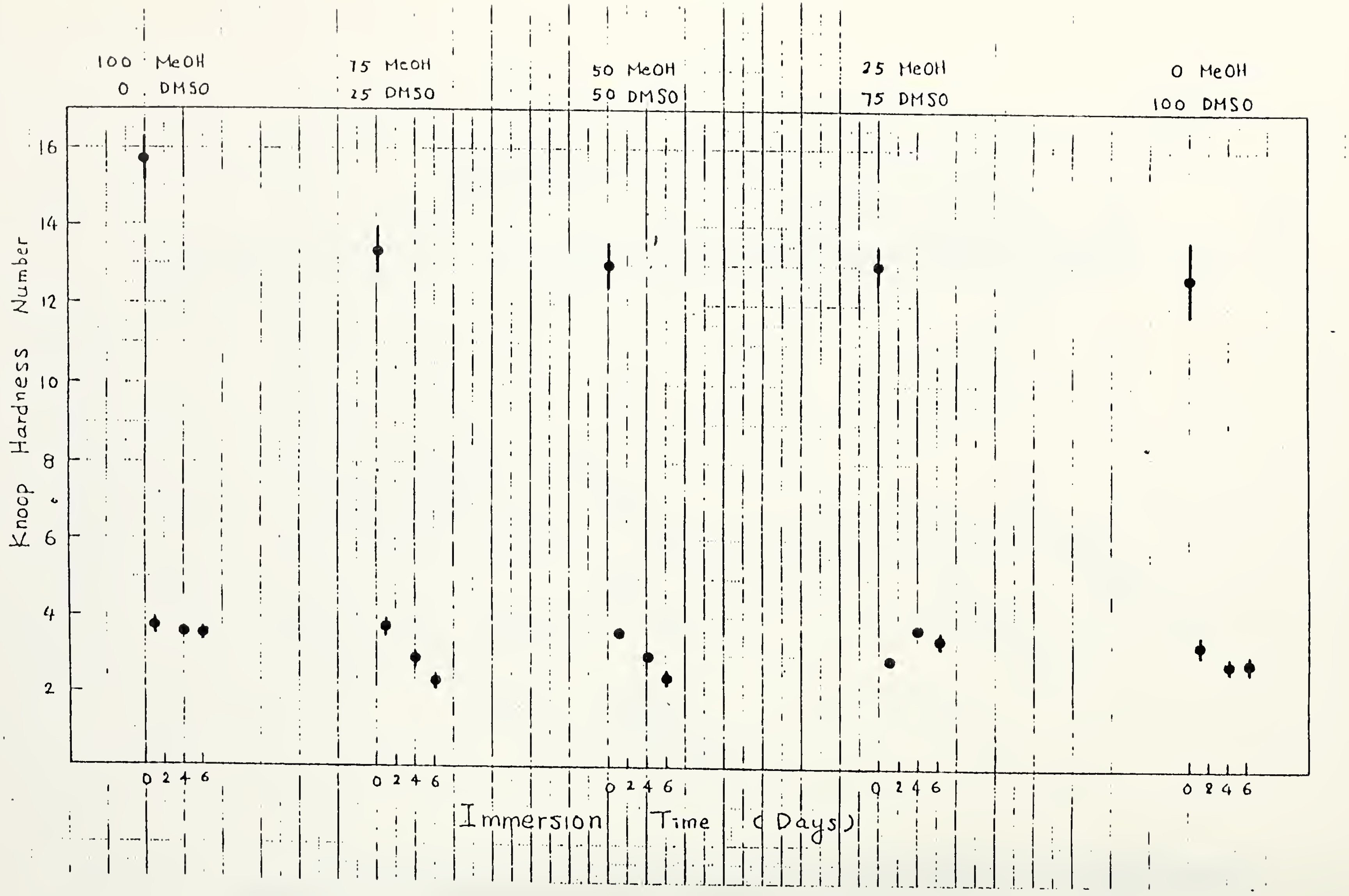


Figure 26. Effect on Knoop Hardness of unfilled BIS-GMA (30% TEGDMA) from immersion in mixtures of methanol and DMSO.

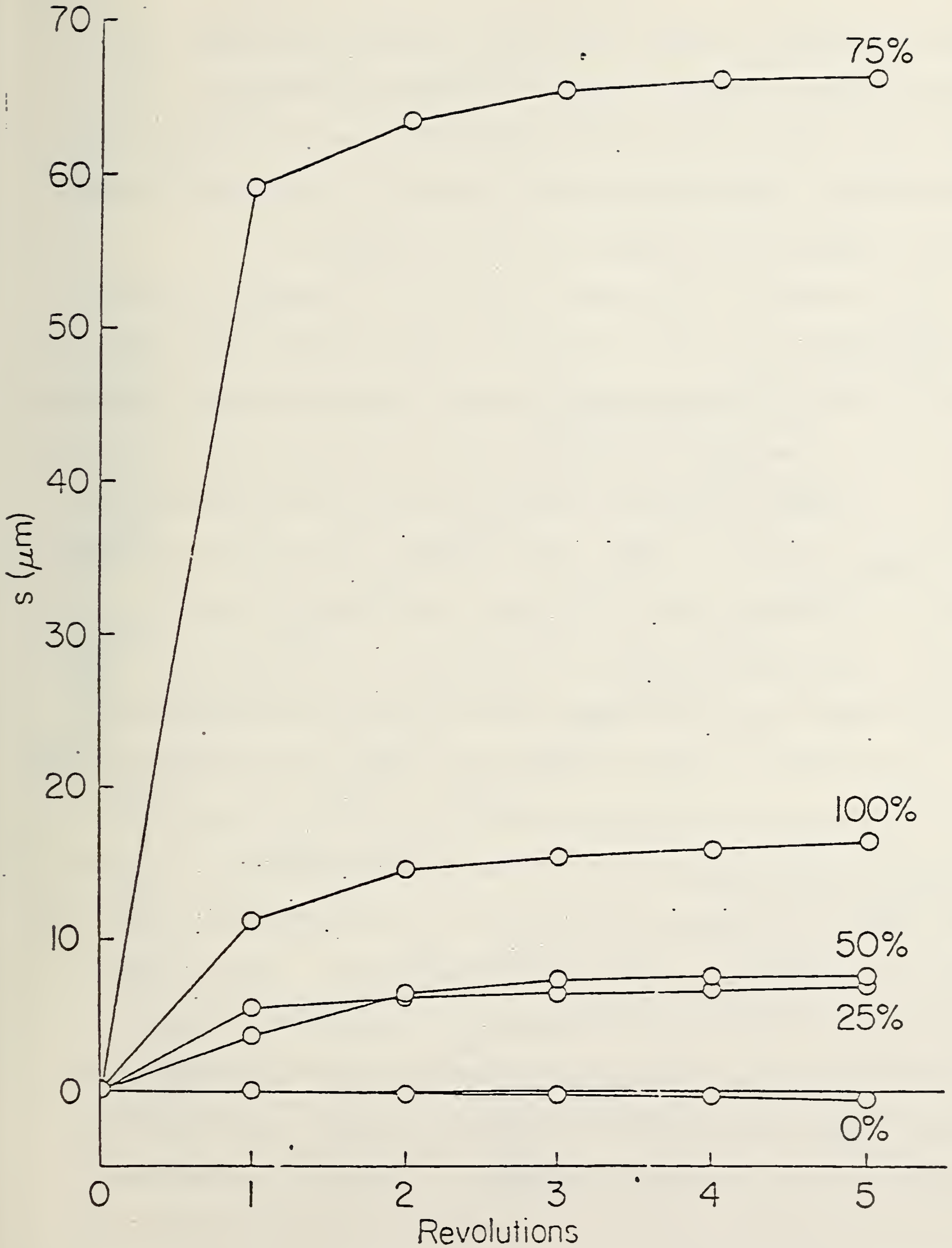


Figure 27. Wear track depth s versus revolutions in indicated ethanol-water solutions.

depths are plotted for each of the first five disc revolutions. The concentrations of ethanol in water are included as parameters. The initial wear rate does not increase monotonically with increasing ethanol concentration. The largest wear shown occurred at 75% ethanol for which 60 μm of composite were removed during the first pass.

The continuation of the wear shown on Fig. 27 extended to 40 hours is illustrated in Fig. 28. The abscissa interval between data points is one hour which corresponds to approximately 1500 specimen disc revolutions. The initial values shown in Fig. 28 are the final ones in Fig. 27. There is a change in the ordering of the wear rates with concentration as the wear progresses. In Fig. 28 the highest wear rate occurs at 100% ethanol in contrast to 75% for the first pass as shown in Fig. 27. This change in ordering is attributed to the higher diffusion rate in BIS-GMA of pure ethanol over that of lower ethanol in water concentrations.

A correlation is obtained between wear after soaking Adaptic specimens in different ethanol solutions and change in hardness of pure BIS-GMA, induced by soaking. Since Knoop hardness involves penetration over only about the first 20 microns of substance, it is appropriate to consider wear over the first five passes for this application. Figure 29 shows the wear (after five passes) plotted against the ratio P_i/P_f where P_i and P_f are the initial average (before soaking) and final (average after soaking) Knoop hardness values as shown in Figure 24. The alcohol-water concentrations are included as parameters. Although the dependences of both wear and hardness ratio are not monotonic with concentration, the deppendence of wear on the hardness ratio is monotonic. In fact, except for the 75% value, nearly linear response is obtained.

A manuscript which includes the results of this activity has been submitted for publication [76].

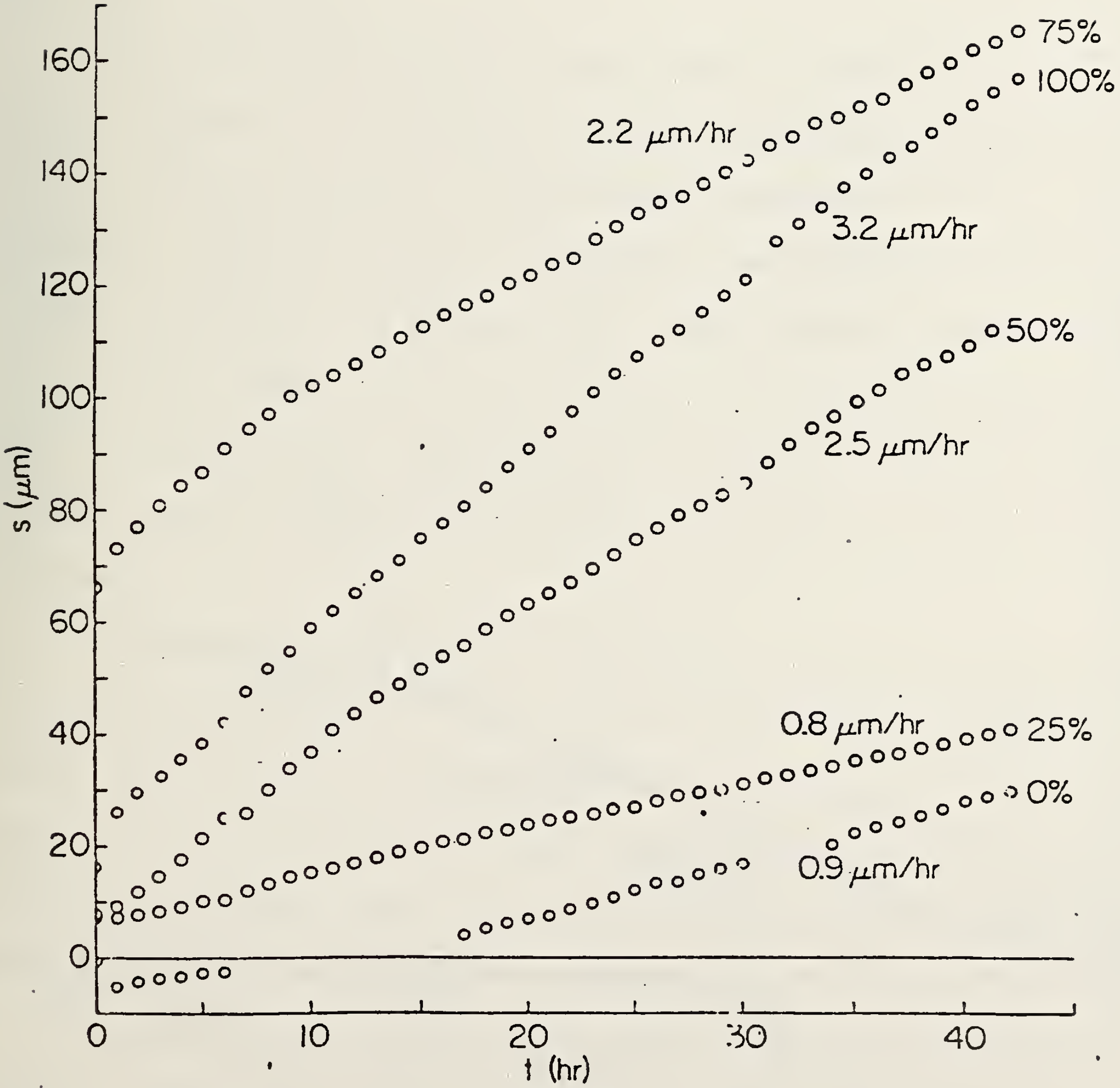


Figure 28. Wear track depth s versus time after extended immersion in ethanol-water solutions. One hour corresponds to 1500 revolutions. The initial data point is the final one in Figure 14.

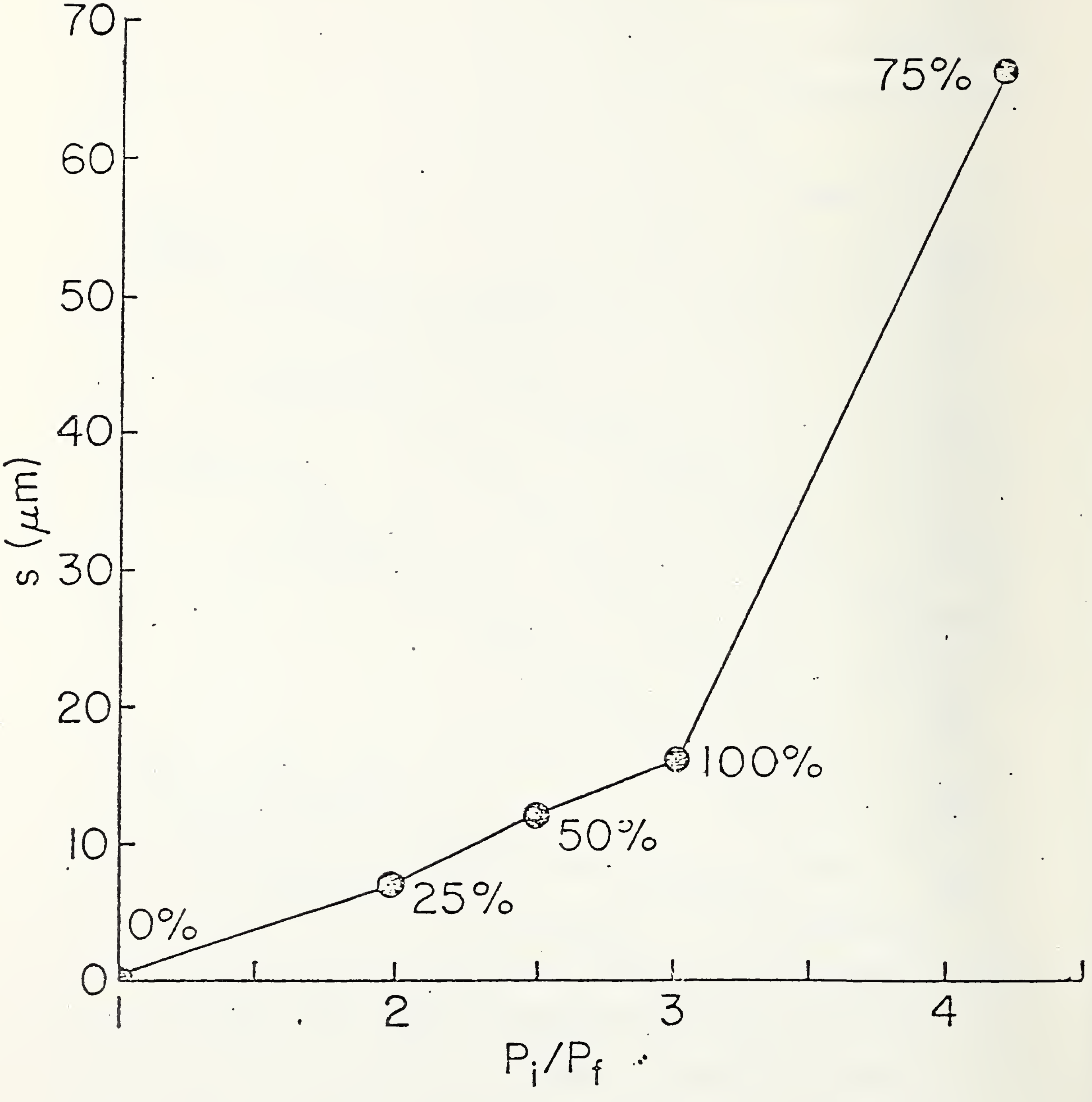


Figure 29. Wear track depth s at five cycles versus hardness ratio P_i/P_f at different indicated concentrations of ethanol in water.

The work on the influence of chemical solvents has been extended to include additional commercial dental composites, in an ongoing activity at the time of this writing. The restoratives being investigated are Profile, which uses a strontium glass filler, Prisma Fil, which is visable light activated, and Adaptic, which is a conventional composite and is used here as a control.

The specimens were stored in the solvents at 37°C for one week prior to the wear tests. Knoop hardness values were obtained during this time. Since we do not completely know the polymer composition of all of these composites, we were not able to do hardness measurements on the pure polymer base as with the previous work. Knoop Hardness Numbers on these composites are difficult to obtain because of the uncertainties which result from whether the indentor strikes a region of filler or polymer. For this reason we obtained the average of 10 hardness velues on each specimen.

Wear measurements were made on specimens previously stored in 0, 25, 50, 75, and 100% ethanol in water solutions, and heptane. Maximum initial wear (after five cycles) was obtained at either 75 or 100% ethanol storing conditions with Adaptic being the largest (38 μm) and Prisma-Fil smallest (5 μm). At all other storing conditions the initial wear of Prisma-Fil was essentially non-existent.

The preliminary results for the three composites are summarized in Fig. 30. The initial wear track depth is plotted against P_f the final Knoop Hardness Number (KHN), obtained after soaking. Hardness values were not obtained on the 25 and 50% ethanol soaked specimens. A common threshold value of surface hardness is approximated for all three composites regardless of the storing conditions. Below this value the initial wear increases

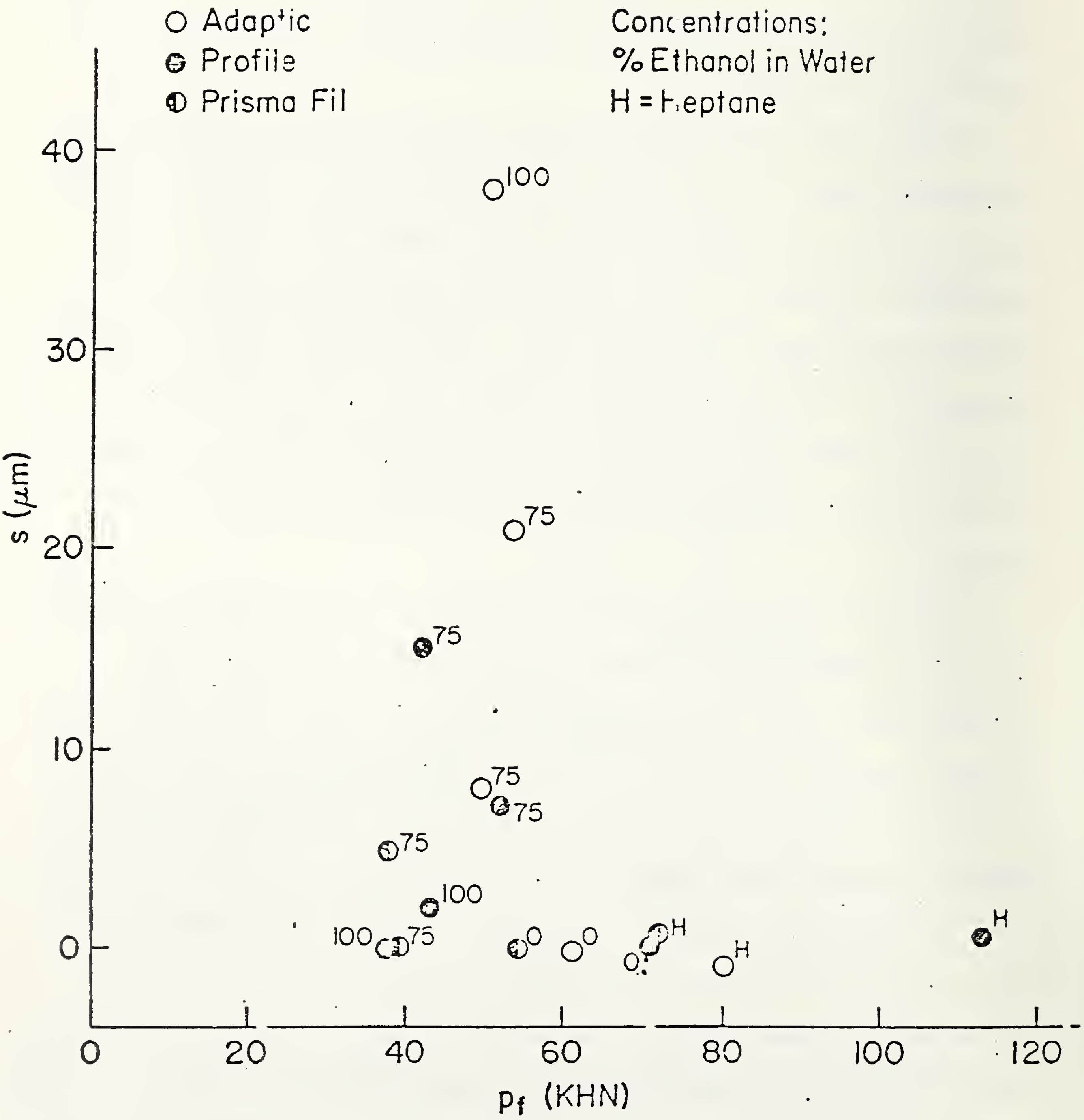


Fig. 30. Initial wear track depths (after 5 cycles) versus final KHN, P_f. Prior to wear test the specimens were stored for one week at 37°C in the indicated solvents.

dramatically with decreasing hardness. Although the Prisma Fil specimens are softened as seen by an apparent decrease in surface hardness with increasing ethanol concentration, its wear resistance remains good in contrast to that for Profile and, in particular, Adaptic.

B. Environmental Effect on Physical Properties of Dental Composite Restorative

1. Changes (Compressive Strength and KHN) in Composites Induced by Thermocycling

The physical properties in terms of the compressive strength and the surface hardness (as reported in III A4) of dental restorative composites were found to be weakened [77] by certain food simulating chemicals chosen in one of the FDA guidelines [74]. All but one of the composites tested herein were immune to attack by acids. Furthermore, thermocycling seemed to cause no negative effect on the physical properties of all the composites tested.

A close examination using scanning electron microscope [78,79] and subsurface damage layer analysis [80] of the worn surfaces of composites pre-immersed in chemicals reveal that stress may not be the only dominant cause of excessive wear observed.

The materials tested included two conventional composites--Adaptic, Concise, one microfill composite--Silar, one strontium glass filled composite--Profile and a visible light cured composite--Prisma. The surface hardness of the specimens were measured using a Knoop hardness tester, each data point reported herein is an average of eight measurements from two specimens. The compressive strength was determined using an Instron machine and each data point represents an average of 2-4 specimens.

Lactic acid [81,82], acetic acid, and phosphoric acid with their pH values maintained at 4.5 were used. The specimens were immersed in these acids at 37°C and were removed at the end of 1, 3, 7, and 15 days to test their physical properties. No significant trend of change in compressive strength was observed in all the acid immersed specimens. All the specimens except Profile showed no change in Knoop hardness measurement results. The data are shown as follows:

TABLE 37. Change of Knoop Hardness Number (KHN) and Compressive Strength (C.S.) in MPa of Dental Composites Caused by Immersion in Acids

<u>Days of Immersion</u> (<u>Adaptic</u>)

		0	1	3	7	15
Acetic Acid	C.S.	172 ±10.0	288 ±14.1	273.5±33.2	245 ±19.1	219.9±23.
	KHN	66.3± 5.5	57.4± 6.3	52.3± 7.0	57.1± 4.8	56.5± 6.
Lactic Acid	C.S.	272 ±10	283 ± 0	289.5±24.8	261 ±11.3	219.9±18.
	KHN	67.5± 4.2	49.6± 3.4	61.6± 4.4	59.7± 4.6	59.5± 3.
Phosphoric Acid	C.S.	272 ±10	271 ± 5.66	273.0±46.5	235.5±21.9	243.5±17.7
	KHN	62.3± 4.6	56.5± 9.5	54.7± 5.0	61.5±10.0	59.0± 4.

<u>Days of Immersion</u> (<u>Profile</u>)

		0	1	3	7	15
Acetic Acid	C.S.	317 ±34.2	302.5±16.3	300 ±24.0	271 ±17.0	290.6±21.
	KHN	78.3±10.0	76.0± 8.6	65.2± 5.5	57.5±24.7	53.1± 7
Lactic Acid	C.S.	317 ±34.2	291 ± 0	259.0±77.8	289.0± 8.5	314.2±18.5
	KHN	71.05± 8.2	62.3± 6.2	59.2± 5.0	56.9± 9.6	54.9± 7
Phosphoric Acid	C.S.	317 ±34.2	315 ±23.6	312.0±19.8	253.5±13.4	314.2±25.9
	KHN	71.8± 8.0	77.6± 8.4	65.4± 3.8	77.2± 4.7	66.6± 9

TABLE 37. (cont'd)

Days of Immersion (Prisma)

		0	1	3	7	15
Acetic Acid	C.S.	336.5±39.3	369 ±22.6	342.5±29.0	349.5±27.6	342 ±29.5
	KHN	59.6± 3.5	57.3± 5.8	43.0± 6.1	56.1± 8.2	53.2± 6.7
Lactic Acid	C.S.	336.5±8.3	310 ± 5.7	333 ±21.5	298.5±10.6	353 ±32.0
	KHN	55.5± 4.6	57.0± 8.1	56.7± 9.4	51.5± 6.5	48.3± 5.7
Phosphoric Acid	C.S.	336.5±39.3	278.5±38.9	342.5±75.7	318 ±17.0	385 ±37.6
	KHN	47.5± 3.9	62.3± 3.4	49.6± 2.8	48.4± 5.6	46.8± 3.4

Days of Immersion (Silar)

		0	1	3	7	15
Acetic Acid	C.S.	290.3±20.9	324 ± 2.8	310.5±27.6	306.3±15.1	287.5± 8.8
	KHN	28 ± 4.8	27.9± 4.0	26.6± 7.8	26.3± 3.7	26.5± 4.6
Lactic Acid	C.S.	290.3±20.9	339.5±19.1	307.5±13.4	270.9± 5.5	322.1±24.2
	KHN	28.6± 4.5	32.01±0.2	30.7± 5.4	28.1± 5.2	30.8± 4.9
Phosphoric Acid	C.S.	290.3±20.9	328 ±14.1	316 ± 8.5	318.1±22.2	322.6±14.3
	KHN	27.1± 6.2	31.4± 8.8	33.6±18.3	32.4± 5.6	27.9±10.5

Days of Immersion (Concise)

		0	1	3	7	15
Acetic Acid	C.S.	270.5± 8.8	268.5±24.8	270 ±26.9	304.5±13.4	322.1±20.5
	KHN	85.9±17.4	75.8±15.2	78.5±17.3	67.2±19.6	69.0±15.8
Lactic Acid	C.S.	270.5± 8.8	270 ± 4.2	286.5±16.3	278 ±15.6	298.5±18.4
	KHN	78.2±14.4	81.3±16.3	106 ±33.6	71 ±16.4	76.7±16.2
Phosphoric Acid	C.S.	270.5± 8.8	276 ± 5.7	273 ±41.0	290.5±10.6	306.4±27.2
	KHN	77 ±11.4	66.5±13.9	102 ±26.2	79.7±10.0	79.2±14.8

The major difference between Profile and the other composites tested is the filler composition; strontium glass was used in Profile but not in the other ones. Therefore, it is reasonable to believe that reactions among strontium glass fillers and the acids gave rise to the weakening of the surface hardness of Profile."

The thermocycling test was carried out by immersing specimens in 5°C and 55°C water baths and cycling at a rate of 540 cycles per day. Specimens were removed at the ends of 1, 3, 6, and 9 days for measuring the physical properties. For all the specimens tested, no significant change of both the compressive strength and the surface hardness was observed. Only the data of Concise will be presented in Table 38, and these data are believed to be representative for all other composites tested:

TABLE 38. Changes of Compressive Strength and KHN of <u>Concise</u> Resulting From Thermocycling (5°C-55°C)

	Cycling Date				
Compressive strength (MPa)	279 ±17.8	268.8±18.0	295.8±14.1	299.8±23.9	284.8±11.5
	0	1	3	6	9
KHN	77.3±10.9	78.8± 9.4	79.3± 5.6	81.5± 4.7	82.7± 9.2

According to one of the FDA guidelines, the following chemicals were chosen for food simulating purposes: acetic acid with $\text{pH} \leq 5.0$ for acidic food, n-heptane for fatty food, ethanol for beverage and pure water. Three additional chemicals were used in the present study to fill the gap of solubility parameters between n-heptane and ethanol; they were methanol, acetone, and ethylacetate.

The composite specimens were immersed in these chemicals at 37°C and removed at the end of 1, 3, 7, and 10 days for the physical properties measurements. The results of Adaptic only will be shown in the following table, and all other composites showed similar behaviors.

TABLE 39. Effects of Different Chemicals on the Compressive Strength and KHN of Adaptic*

		Immersion Date				
		0	1	3	7	11
n-heptane	C.S. (MPa)	270.8± 8.4	269.3±14.5	278.3±20.5	291.3±20.5	283.0±13.5
(7.4)	KHN	73 ±21.4	70.0±15.9	80.1±11.0	75.3±17.4	86.7±24.6
Ethylacetate	C.S.	280.0±20.1	247.0±26.2	236.0± 2.7	233.0±20.5	230.0±19.6
(9.1)	KHN	67.2±14.1	43.4± 5.7	43.0± 7.9	48.4± 9.5	41.1± 2.8
Acetone	C.S.	230.0±26.5	203.0± 5.0	178.0±30.1	142.0±15.6	134.0± 9.9
(9.9)	KHN	56.5± 7.6	39.2± 2.7	31.3± 2.8	30.0± 2.1	30.6± 2.5
Ethanol	C.S.	258.0±20.3	246.0±33.9	225.0± 5.0	250.0±14.9	208.0±33.9
(12.7)	KHN	60.5±14.6	48.2±13.4	44.0± 8.9	35.0± 4.8	35.1± 5.9
Methanol	C.S.	230.0±28.6	202.0± 3.5	213.0± 5.7	179.0± 6.4	152.0±18.0
(14.5)	KHN	63.5± 5.1	36.7± 5.3	36.6± 2.2	32.7± 5.4	32.0± 2.7
Water	C.S.	277.0±14.1	288.0±14.2	282.0±23.2	264.0± 7.1	207.1±17.6
(23.4)	KHN	62.4± 4.5	57.4± 9.8	54.7± 6.0	60.6±10.1	58.9± 5.3

*The number listed under each solvent is the value of its solubility parameter in terms of $(\mathrm{cal/cm^3})^{1/2}$.

These data indicate that chemicals with solubility parameters between those of n-heptane and water will soften Adaptic. Furthermore, the Knoop hardness test seems to be a more sensitive one in detecting the property change than the compressive strength test.

A more complete study on the softening of BIS-GMA based dental composites by chemicals with different solubility parameters has been finished, the results have been submitted for publication [77]. The effect of the chemical softening on the wear resistance of some dental composites was discussed in the foregoing section (III A4).

The softening rate of dental composites by any given chemicals was found to depend on the curing temperature, hence the degree of the Knoop hardners number of any given composite by chemical softening could be fitted by a simple equation relating the KHN with the immersion time t as

$$\text{KHN} = (\text{KHN})o \exp(-Dt)$$

The values of $(\text{KHN})_o$ and D for both Adaptic and Prisma cured at 37°C and 100°C are listed in Table 40.

TABLE 40. Initial Knoop Hardness Number $(\text{KHN})_o$ and Time Constant D. of Dental Composites as A Function of Curing Temperature T_c

	T_c(°C)	$(\text{KHN})_o$	D(Day^{-1})	Chemical
Adaptic	37	53.9	0.051	Ethanol
Adaptic	100	79.5	0.025	Ethanol
Adaptic	37	58.2	0.29	Methanol
Adaptic	100	68.4	0.051	Methanol
Adaptic	37	59.4	0.12	Ethyl Acetate
Adaptic	100	83.9	0.031	Ethyl Acetate
Adaptic	37	44.7	0.050	Acetone
Adaptic	100	80.2	0.044	Acetone
Prisma	37	46.1	0.030	Ethanol
Prisma	100	61.0	0.028	Ethanol
Prisma	37	48.0	0.113	Methanol
Prisma	100	59.9	0.039	Methanol
Prisma	37	49.5	0.039	Ethyl Acetate
Prisma	100	66.3	0.018	Ethyl Acetate
Prisma	37	44.4	0.035	Acetone
Prisma	100	57.8	0.029	Acetone

The data shown above indicate that the softening rate changes not only with the curing temperature as expected, but also changes with the composites used. Prisma seems to have a lower softening rate for all the chemicals tested.

2. Investigation of *In Vivo* Wear Mechanism of Dental Composite Restorations

Nine biopsy specimens have been received from Dr. S. Moffa and Ellison of U.S.P.H.S hospital at San Francisco. A special technique of obtaining thin sections from dental composites has been developed. Transmission optical micrographs were obtained from the silver stained thin sections of these biopsy specimens. The results clearly demonstrate that the defects within the damaged sublayer beneath the wear surface are located throughout the polymer matrix instead of being confined at the filler matrix interfaces. An example is given in Fig. 31 which is a transmission optical micrograph from a 2^+ year old Adaptic restoration. The polymeric matrix within the damaged sublayer was uniformly stained by silver particle indicating creation of defects throughout the matrix.

A theoretical development of the small angle x-ray scattering (SAXS) in three phase (filler, matrix and microcrack) systems has been completed and this work will be presented at both '81 APS meeting in New Orleans and '82 IUPAC meeting in Amherst, Mass. Both volume concentration and the characteristic length of the microcracks within the damaged sublayer can be determined from SAXS data using this theoretical development.

A quantitative study of the microdefects within the damage layer using a small angle x-ray scattering technique (SAXS) is in progress. One example of the results will be given.

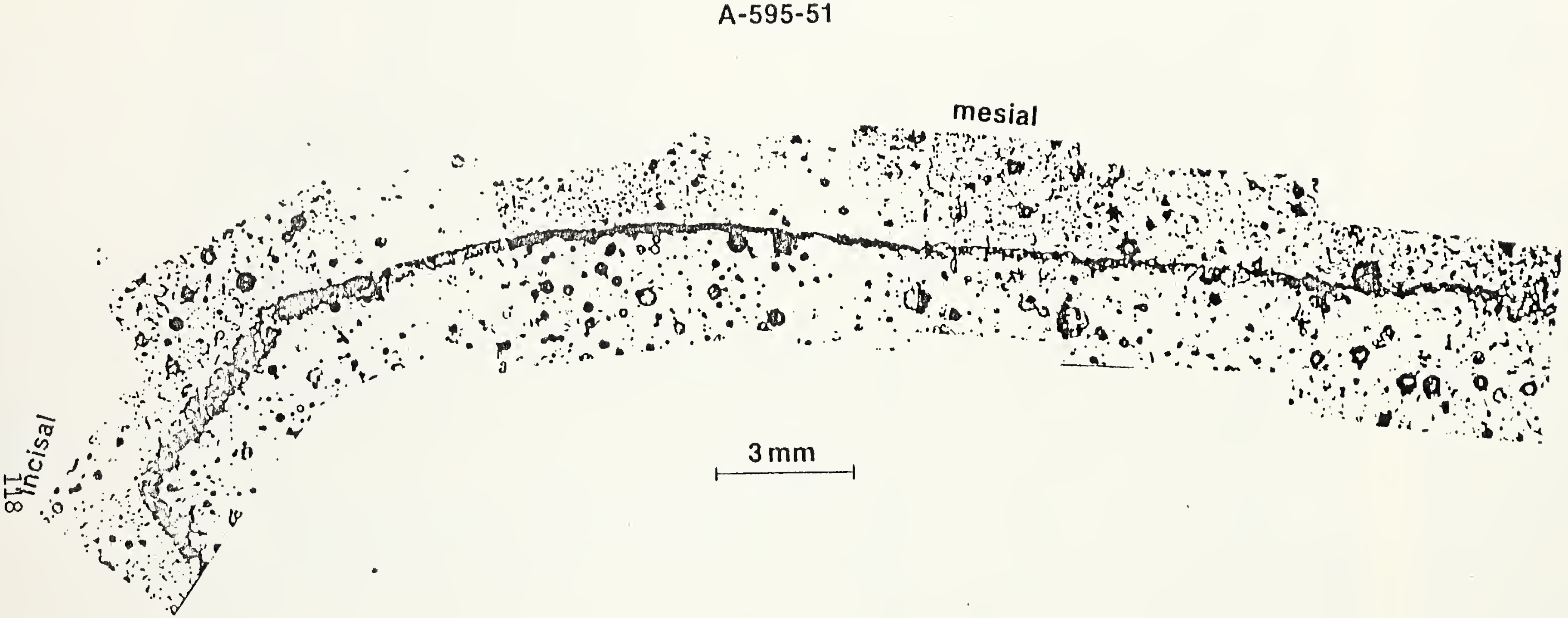


Fig. 31. Combined transmission optical micrographs revealing damaged sublayer of a 2^+ year old in vivo specimen of Adaptic.

A profile restoration removed from a second molar after 13 months clinical service was examined. The x-ray scattering intensity was calibrated with a 1.5% vol. LUDOX solution as a standard reference. The main beam intensity was monitored and integrated throughout the whole measurement. The average volume concentration of the microdefects within a 200 μm layer beneath the occlusal surface was determined to be 0.092% using the density of the strontium glass filler within this specimen as 3.5 g/cm^3. The corresponding values of the volume concentration of the microdefects are 0.113% and 0.072% if the strontium glass density were assumed to be 3 and 4 g/cm^3, respectively.

The linear dimensions of the microdefects within the specimen were found to be isotropic judged from the uniform azimuthal distribution of the scattered x-ray intensity. Furthermore, by using a modified Porod's scheme the average value of the dimension of the microdefects was determined to approximate 40 Å. Both the theoretical and the experimental work of SAXS in composites will be described in manuscript form in the near future.

A microdefect analysis by small angle x-ray scattering technique was carried out on compression fatigued composite restorative material (Profile). The specimen was fatigued with 5000 cycles half sine compressive stress at 60% of its compressison strength. The specimen was then sectioned and examined with SAXS technique. The results can be summarized as follows:

volume concentration of microdefects: 0.32% ($\rho_{\text{strontium glass}} = 3.5$)

average linear dimensions:

parallel to compressive stress: 226 Å

perpendicular to compressive stress: 181 Å

The data shown above on the in vitro specimen suggest that the damage accumulated inside the in vivo specimen is not likely caused by a compression fatigue process. Similar work using SAXS was also conducted on a Profile specimen worn by pin-disc equipment with 10 MPa normal load. The volume concentration of the microdefects within this specimen was found to be too low to be detected by SAXS.

IV. Dental Alloys and Ceramics

Stable prices, lower costs, and often superior properties have resulted in an almost monotonically increasing use of nonprecious and low precious metal alloys at the expense of gold alloys for fixed partial dentures. Experience with these alloys for porcelain veneered prostheses has indicated [83] that due to the lack of fundamental knowledge regarding these systems, problems have been encountered clinically and in the laboratory. Residual stress in porcelain from cooling after firing is thought to be a primary factor leading to failures; precise universally agreed-to techniques for assessing compatibility do not yet exist. A simple, convenient porcelain metal bond test needs to be developed for product development, industrial quality control, and use by standards committees. Methodology for optimizing and controlling casting conditions in the laboratory are also needed, as are techniques to assess the ability of solders to produce acceptable joints for dental applications. The question of how to prepare patterns of fixed partial dentures to obtain multi-unit castings which give the best obtainable fit has only recently begun to be addressed in depth; continued work in this area is needed. The following sections summarize progress which has been made toward addressing these problems and indicates directions for future studies.

In addition to dissemination of research results at IADR and Biomaterials Society meetings (as is indicated in the following material), invited papers will be presented at the AIME Annual Meeting (Recent Developments in Metals as Bio/Dental Alloys: Tesk, Waterstrat, Hinman, and DeRijk), and a Symposium on Finite Element Methods (FEM) and Analysis Techniques (Applications of FEM in Dentistry: Widera, Tesk, Munir, and Hinman) in conjunction with the International Congress on Technology and Technology Exchange in Pittsburgh, February 1982. A chapter on Porcelain/Alloy Fixed Partial Dentures has also been invited for inclusion in a revised edition of Advanced Restorative Dentistry by Lloyd Baum and Richard McCoy.

A. Porcelain/Alloy Stress Compatibility; Residual Stress:

As previously described [84,85], many factors are involved here. Ultimately, a combined materials approach is indicated (for example, see Bertolotti [86] and Fairhurst [87]). The program at NBS is using the analysis of gap changes in a porcelain veneered split metal ring subjected to laboratory firing schedules as the first step toward assessing compatibility and as a technique which might find acceptance as a standard method of evaluation. Both experimental and theoretical methodologies are employed and considered as necessary compliments. For the mathematical modeling, knowledge of numerous physical and mechanical properties are required; some may not be critical to the problem at hand, others very definitely are.

Theoretical calculations completed during the past year have shown that knowledge of the precise value of Poisson's ratio is not critical to either evaluation of stress or of correlation of theoretical and experimental values for gap changes. The calculation of residual stress is, however, very dependent on accurate measurement of the elastic modulus. The determination of this value for different porcelains is planned as part of future studies. (This was originally scheduled for FY81; before proceeding, however, theoretical assessment of the contribution of all measurable parameters was deemed appropriate to provide guidance for experiments). This analysis showed quite clearly that no direct correspondence in magnitudes or locations of maximum shear, tensile (compressive), tangential and radial stresses exists; this is important in consideration of stress relaxation and changes of the glass transition temperature (Tg) as affected by cooling and stress. The finite element technique is the only method known which is capable of handling these affects in a pointwise manner with the complexities involved. (A manuscript [88] on this was presented at the IADR March 1981 meeting).

Another question pertaining to sensitivity of experimental measurements of gap change to changes in properties of the porcelain-metal interface was addressed. The results of this theoretical study were presented at the IADR March 1981 meeting [89] and showed that for the porcelain/alloy thickness ratios being employed experimentally, i.e., $t_{porcelain}/t_{alloy} \geq 1$, interfacial effects may be neglected. This <u>is</u> <u>not</u> the case under some conditions as was shown.

One of the prime properties needed for theoretical analysis of the gap change is the temperature dependence of the shear viscosity (for stress relaxation/retention near Tg). This property was determined for several dental body porcelains (Table #1). Although the viscosity, η, was not measured directly, it was found from the results of others [90] and expansion measurements which were conducted that a close correlation exists between the strain point and the temperature, obtained upon heating, of maximum rate of recovery of quenched excess volume for previously, rapidly cooled expansion specimens. This was reported at the IADR Meeting, March 1981 [91].

Efforts are under way to develop knowledge of other properties which may be deemed necessary for the complete experimental, theoretical analysis of the gap changes. A sensitivity study is being conducted to determine how precisely heat transfer properties are needed. Measurements of elastic modulus are planned (1982-83). Finite element computor models and programs are being developed (1982-83). Ultimately, correlations between experiment and theory will be sought (1983-84). Additional viscoelastic properties are to be determined (1982-83). To render the ring work more germaine as a these affects in a pointwise manner with the complexities involved. (A manuscript [88] on this was presented at the IADR 1981 March meeting). The results of another set of calculations were presented at the IADR March 1981 meeting [89] and showed that for the porcelain/alloy thickness ratios being employed experimentally, i.e., $t_{porcelain}/t_{alloy} \geq 1$, interfacial effects may be neglected. This is not the case under some conditions as was shown.

One of the prime properties needed for theoretical analysis of the gap change is the temperature dependence of the shear viscosity (for stress relaxation/retention near T_g. This property was determined for several dental body porcelains (Table 41). The viscosity, η, was not measured directly. The results of others [90] and expansion measurements which we conducted showed that a close correlation exists between the strain point and the temperature corresponding to the maximum rate of recovery of quenched excess volume for previously, rapidly cooled expansion specimens. This was reported at the IADR Meeting, March 1981 [91].

Efforts are under way to develop knowledge of other properties which may be deemed necessary for the complete experimental and theoretical analysis of the gap changes. A study is being conducted to determine the required levels of accuracy and precision that are needed in the values for the heat transfer properties. Measurements of elastic modulus are planned (1982 - 1983). Finite element computer models and programs are being developed (1982 - 1983). Ultimately, correlations between experimental measurements and theoretical determinations will be sought (1983-84). Additional viscoelastic properties are to be determined (1982-83). To render the ring work more germane as a standardized

Table #41

Activation Energy, Q, for Deformation of 1 st Fire-Body Porcelains

Porcelain	Q KJ/mol	Kcal/mol
a. Vita VMK-68	354 ± 43	84.5
b. Biobond	336 ± 36	80.3
c. Micro Bond	322 ± 10	77.0
d. Will-Ceram	362 ± 13	86.5
e. Ceramco	318 ± 5	75.9
f. Neydium	216 ± 150	51.7

compatibility evaluation, finite element models of crowns, bridges, etc., will be developed, using the properties and techniques which will have been shown to provide agreement between theoretical and experimental studies of the gapped rings (1984-86). One abstract [92] of a sensitivity study of the behavior of a split metal ring with variable heat transfer properties was submitted for the 1982 annual meeting of the IADR.

B. Porcelain-to-Alloy Bond Strength

Numerous porcelain-to-metal bond tests have been proposed over the year, yet a simple, expedient, quantitative test has not been devised. A major drawback is the fact that most proposed test methods utilize testing under shear conditions. This has a number of detriments but perhaps the most stringent one is that brittle materials (porcelain) fail in tension. Other problems are that the preparation of specimens is often time consuming. A test methodology is under development which utilizes the principle of development of uniform tensile stresses in layers of a uniform cross-section beam subjected to pure bending. Along an alloy beam, (elastic modulus, E_m), longitudinal sections have layers replaced by a different material (porcelain) of elastic modulus, E_p. The neutral layer of these sections shifts with changes in E_p. Calculations show for $1 \lesssim n \lesssim 2$ ($n = E_m/E_p$) porcelain can comprise from 50 to 80% of beam thickness, t, without altering the stress distribution significantly. Upon application of a force, F, fracture occurs either at the porcelain fracture stress (PFS) in porcelain or at the porcelain-metal bond strength (PMBS) at the interface. The fracture stress,

$\sigma_f (\sigma_f = \sigma_{PMBS}$ or $\sigma_{PFS})$ is given by

$$\sigma_f = \frac{6F\ell(t-\bar{y})}{w[b^3 + nc^3 + 12(b(c+b/2)-\bar{y})^2 + nc(c/2-\bar{y})^2)]}$$

where $\bar{y} = \frac{1}{2}\,\frac{t^2+c^2(n-1)}{t + c(n-1)}$, b = section thickness of porcelain, c = section thickness of metal, w = beam width. For the dimensions of specimens tested

(62 x 11 x 3 mm), and for 1.5 mm thick porcelain sections, $\sigma_f = 72.5F$ for n=1 and $\sigma_f = 62.0F$ for n=2.

The ease of specimen preparation and the non-sensitivity of results to porcelain thickness render the test specimen design and methodology as potentially attractive for use as a generalized adhesive bonding test. Detailed stress analysis on general systems will be explored via simple engineering mechanics as well as finite element analysis (1982-83), with consideration for determination bonding of hard tissue (enamel or bone) to adhesives or alloplastic surgical implants (1982-84). Experimental studies and statistical analysis of several dental porcelain/alloy combinations are planned with examination of potential usefulness of 3 point loading (also possible with the specimen design under consideration, symmetrical about the mid-section) (1982-84). Development of a master mold pattern for casting of alloy specimens should be completed in 1982. Two abstracts [93, 94] on this methodology were submitted for the 1982 annual meeting of the IADR.

C. Castability Evaluation

Studies continue on the use of the castability value as determined by the use of a polyester grid pattern in cast alloy (presented at the 1981 annual meeting of the IADR) [95]. (Completed cast segments are counted and the percentage of such segments is referred to as the castability value, cv). The effects of superheat (over alloy liquidus) and mold temperature were investigated. Preliminary results indicated optimum casting temperature (superheat) and mold temperature may be determined and that these are not always coincidental with manufacturers' instructions. Optimum castability is seen to be accompanied by higher predictability, i.e., smaller standard deviation for the cv.

The cv is also dependent on the investment brand which is used. Studies will continue, extended to other alloy systems and investments to determine if the behavior observed thus far is universal in nature (1982-83). Effects of cast grid size variations on the cv are also planned (1982-85 to assess effects and the benefits from using certain grids to delineate certain features of castability for correlation with observed practical results . For example, is a finer grid useful for predicting sharpness of cast margins?; is a heavier grid useful for hot tearing and so on. Determination of castability phase diagrams will be considered. A manuscript [96] on progress of this work was submitted for the 1982 annual meeting of the IADR.

D. Fit and Soldering

Among the most complex phenomena involved are the fit of cast multiple unit fixed partial dentures (MUFPD'S) and the joining of multiple sections before and after porcelain application, and the effects of porcelain application itself on fit. Preliminary results [97] (presented at the 1981 annual meeting of the IADR) showed that variability could be reduced (predictability increased) for MUFPD'S if an all wax sprue and runner bar system were used relative to using wax sprues and gates and a plastic runner bar. Moreover, a bench setting technique was found to be desirable relative to a hygroscopic technique (the latter is consistent with numerous observations reported in the dental literature). This study is only in the initial stages, and effects of ring sizes and types, investments, and techniques are planned with effects of sectioning and joining and effects of porcelain application are planned for the next several years (1982-86). The objective is to determine optimal conditions/techniques for producing sound MUFPD'S. The effects of the porcelain application phase on fit will be examined for correlation with opening and closing of gaps of split metal ring porcelain/alloy combinations.

E. Fluorescing Agents and Master Frits for Dental Porcelains

Studies had been proposed to examine the need for new fluorescing agents for dental porcelains, in particular with regard to combined esthetics (translucency plus color plus intensity) and preparation of master fluorescing compounds. Techniques for preparation of master frits which may be used in place of mixed feldspar are also under consideration. Work in these areas is projected in cooperation with the ADAHF unit at NBS. Progress in these areas has been temporarily suspended to allow a more concentrated effort on commercial porcelain/alloy studies described throughout the preceeding pages of this report.

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Invited Talks (1981)

Adhesion to Tooth Structure. G. M. Brauer. Session on Biomedical Adhesion, Adhesion Society, Savannah, Ga.

Dental Materials Research at NBS. J. Cassel. Georgetown Dental School Special Topics, Seminar Program, Washington, D. C.

Evaluation of Dental Porcelain and Alloy Characterization. John A. Tesk. Johnson and Johnson Dental Research Center, East Windsor, New Jersey.

Factors Influencing Selection of F.P.D. Alloys. J. A. Tesk and R. W. Hinman. American Association of Dental Schools, Annual Meeting, Biomaterials Group.

Current Concepts in MetalPorcelain Systems. R. A. Hinman and J. A. Tesk. The University of Texas, Teleconference Network of Texas, Washington, D. C.

Abstracts IADR/AADR Meeting, March 81, Chicago, on Microfilm

Effects of Porcelain/Alloy Interfacial Diffusion Zones on Thermomechanical Strain. Abstract 508, J. A. Tesk, R. W. Hinman[1], G. E. O. Widera[2], J. M. Cassel, and A. D. Holmes.

Fit of Multiple Unit Fixed Partial Denture Castings. Abstract 262, R. W. Hinman[1], J. A. Tesk, E. E. Parry[1].

Cements from 2,5Dimethoxyphenol and Zinc Oxide. Abstract 249, J. W. Stansbury, H. Argentar[3] and G. M. Brauer.

Degree of Polymerization of Dental Resins by Differential Scanning Calorimetry. Abstract 234, J. M. Antonucci and E. E. Toth.

Influence of Chemicals on *In Vitro* Wear of Dental Restorative Composites. Abstract 243, W. Wu and J. E. McKinney.

Theoretical/Experimental Studies of Stress Compatibility in Porcelain-Veneered Split Metal Rings. Abstract 838, G. E. O. Widera[2], J. A. Tesk, R. P. Whitlock[1], R. W. Hinman[1], E. E. Parry[1].

Application of Silane Coupling Agent to Inorganic Components of Composites. Abstract 235, T. M. Chen[4] and G. M. Brauer.

Peroxy Esters and Hydroperoxides as Initiators for Composite Resins. Abstract 49, G. M. Brauer and J. W. Stansbury.

Relationship Between Subsurface Damage and Wear of Dental Restorative Composites. Abstract 1095, J. E. McKinney and W. Wu.

Effect of Hygroscopic Diluents on the Properties of Cured Composites. Abstract 236, K. Dermann, N. W. Rupp[3] and G. M. Brauer.

A Practical Test to Evaluate the Castability of Dental Alloys. Abstract 374, R. P. Whitlock, R. W. Hinman[1], G. T. Eden[1], J. A. Tesk, G. Dickson, and E. E. Parry[1].

Temperature Dependence of Shear Viscosity for Several Dental Porcelains. Abstract 839, J. A. Tesk, R. W. Hinman[1], R. P. Whitlock[1], A. D. Holmes, E. E. Parry[1].

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Papers Published (FY81)

Effect of Diluent Monomer on the Physical Properties of BISGMAbased Composites. D. Dulik[1], R. Bernier[1], and G. Brauer. J. Dent. Res. 60, 983-89 (1981).

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The Accelerative and Adhesive Bonding Capabilities of Surface Active Accelerators. J. Antonucci, D. Misra[2], and R. Peckoo[1]. J. Dent. Res. 60, 133242 (1981).

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Consideration of Some Factors Influencing Compatibility of Dental Porcelain/Alloy, Part II, Porcelain/Alloy Strain. J. A. Tesk, R. P. Whitlock[4], G. E. O. Widera[5], A. Holmes, and E. E. Parry[4], Precious Metals, Proceedings of the 4th International Precious Metals Institute Conference, Toronto, Ontario, Canada, June 1980, Pergamon Press (1981).

Solder and Fluxes. J. A. Tesk. Dentists Desk Reference, Materials, Instruments and Equipment, First Edition, American Dental Association Publications (1981).

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The following manuscripts are under NBS editorial review or have been submitted for publication:

Intraoral Secondary Radiation Dose from Neutron Activated Dental Materials. J. A. Tesk, R. P. Whitlock[1], and A. Holmes.

Theoretical/Experimental Studies of Stress Compatibility in Porcelain-Veneered Split Metal Rings. G. E. O. Widera[2], J. A. Tesk, R. W. Hinman[1], N. Munir[3].

Physical Metallurgy of Dental Casting Alloys. J. A. Tesk and R. M. Waterstrat.
(Parts C; CoCoMo System
D; NiCr System
E; Fe and Austenitic Steels
F; Titanium Alloys.

Effects of Porcelain/Alloy Interfacial Diffusion Zones on ThermoMechanical Strain. J. A. Tesk, R. W. Hinman[1], G. E. O. Widera[2], A. D. Holmes and J. M. Cassel.

Application of Small Angle Xray Technique to Damaged Particulate Reinforced CompositesA Theoretical Treatment. W. Wu.

Apparatus for Measuring Wear of Dental Restorative Materials. J. McKinney.

Effect of Hydrophilic Diluents on the Properties of Cured Dental Composites. K. Dermann[4], N. Rupp[5], and G. Brauer.

Extent of Polymerization of Dental Resins by Differential Scanning Calorimetry. J. Antonucci and E. Toth.

Relationship Between Subsurface Damage and Wear of Dental Restorative Composites. J. McKinney and W. Wu.

Influence of Chemicals on *in vitro* Wear of Dental Restorative Composites. W. Wu and J. McKinney.

Cements from 2,5Dimethoxyphenol and from Hexyl VanillateOEthoxyBenzoic Acid and Zinc Oxide. J. Stansbury, H. Argentar[5], and G. Brauer.

Peroxy Esters and Hydroperoxides as Initiators. G. Brauer and J. Stansbury.

The Softening of BISGMA Base Polymer by Chemicals with Different Solubility Parameters. W. Wu, J. Pestaner[6], and R. Bowen[5].

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Abstracts Submitted for 1982 AADR/IADR Meeting

Cements Containing Vanillate Esters, EBA and Zinc Oxide. G. M. Brauer and J. W. Stansbury[1].

Dental Resin and Initiator Systems Based on Polythiols. J. M. Antonucci, J. W. Stansbury[1], and D. J. Dudderor[2].

Subsurface Wear Defects Analysis of Both *In Vivo* and *In Vitro* Dental Restorative Composites. W. Wu, E. Toth, and J. P. Moffa[3].

Influence of Chemical Softening on Wear of Three Types of Dental Composites. J. E. McKinney and W. Wu.

Use of a Castability Test for Optimizing Mold and Casting Temperature. R. W. Hinman[4], J. A. Tesk, R. P. Whitlock[4], E. E. Parry[4] and J. S. Durkowski[4].

A Quantitative/Expedient PorcelaintoMetal Bond Test; Part I, Theoretical Basis. J. A. Tesk, G. E. O. Widera[5], R. W. Hinman, and W. Derijk[6].

A Quantitative/Expedient PorcelaintoMetal Bond Test; Part II, Preliminary Results, W. G. Derijk[6], J. A. Tesk, R. W. Hinman[4], E. E. Parry[4], M. Conner[8], and G. E. O. Widera[5].

Effect of Thermal Parameters on Compatibility in Porcelain Veneered Split Metal Rings. G. E. O. Widera, N. Munir[7], J. A. Tesk, and R. W. Hinman[4].

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Abstracts Submitted for Biomaterials Society Meeting, 1982, Orlando, FL

On the Compatibility of Dental Porcelain Metal Alloy Systems.
G. E. O. idera, J. A. Tesk, N. Munir, R. W. Hinman, and W. Derijk.

Environmental Effect on Physical Properties of Dental Composite Restoratives
W. Wu and J. Pestaner

Additional Abstracts, FY82

Recent Developments in Metals as Dental Bio/Alloys. J. A. Tesk, R. W. Hinman, R. Waterstrate, and W. Derijk. Symposium on Recent Developments in Biological Alloys, AIME

Small Angle X-ray Analysis Applied to Three Phase Composite Systems.
W. Wu. IUPAC and Am. Phys. Soc.

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 81-2431	2. Performing Organ. Report No.	3. Publication Date December 1981

4. TITLE AND SUBTITLE

Properties and Interactions of Oral Structures and Restorative Materials

5. AUTHOR(S) J. M. Cassel, J. A. Tesk, G. M. Brauer, J. M. Antonucci, W. Wu, J. E. McKinney, R. W. Hinman

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.
Y01-DE-40015

8. Type of Report & Period Covered
Annual Report
10/1/80 - 9/30/81

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

National Institute for Dental Research
National Institutes of Health
Westwood Building, Room 506
Bethesda, MD 20205

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

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

New dental cements that overcome major shortcomings of zinc-oxide-eugenol type materials were formulated. The new cements, based on esters of vanillic acid or its isomers, do not inhibit polymerization of methacrylate resins that they contact and have improved strength and solubility properties over previous cements. The softening of dental composites by chemical solvents selected for food simulation was demonstrated to directly affect their wear performance as measured with a classical pin (stainless steel) or disc (composite) wear apparatus. Wear resistance following immersion of the composites in ethanol/water solutions correlated with changes in hardness as a result of the immersion. Small angle x-ray scattering (SAXS) Analysis has yielded information on the volume concentration and characteristic length of microcracks in both in vitro and in vivo worn composite specimens. Theoretical calculations showed that for the porcelain/alloy thickness ratios (i.e. ≧ 1) being employed experimentally, interfacial effects could be neglected for the split ring gap change (compatibility) analysis and a knowledge of a precise value for Poisson's ratio was not required for accurate assessment of residual stresses. (A castability test was refined to the point that a castability value can be determined for any given dental alloy.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Castability; cements; compatibility; composites; polymerization; porcelain/alloy; and wear resistance.

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☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES
159

15. Price
$14.00