

## Investigation of Fast-Setting Acrylic Adhesives for Bonding Attachments to Human Tooth Surfaces

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### Synopsis

Some of the problems encountered in adhesive bonding of plastic attachments to human tooth surfaces were investigated. Acrylic adhesives based on poly(methyl methacrylate)-methyl methacrylate monomer mixtures with benzoyl peroxide initiation and *N,N*-dimethylaniline acceleration were utilized. Both homopolymers and copolymers were investigated. Recently extracted upper central incisors were employed in the bonding experiments. Bond strengths were improved by pretreating the tooth surfaces with mineral acids such as  $H_3PO_4$ . Surface wetting by the liquid adhesive was shown to be improved by the acid treatment. The molecular weight of polymer or copolymer employed in the liquid adhesive had an important effect on bond strengths. The optimum molecular weight for obtaining maximum bond strengths was around 20,000 g./mole. Water immersion of the bonded specimens at 37°C. for periods up to 6 weeks had a deleterious effect on bond strengths. Nevertheless, it was shown that some of the adhesives formed reasonably strong bonds for periods exceeding 6 months even with water immersion.

In a previous publication<sup>1</sup> we reported on some preliminary work on bonding plastic orthodontic attachments to human tooth surfaces. The uses of such an adhesive system in orthodontics has been discussed previously,<sup>1-3</sup> and we wish to confine our attention specifically to some of the problems we have encountered in utilizing fast-setting acrylic adhesive systems for bonding plastic attachments to human tooth surfaces. Although we have investigated other adhesives (epoxy resins, cyanoacrylate, and others), we have recently focused our attention mostly on systems containing homopolymers and copolymers of methyl methacrylate. We have done this primarily for the following reasons: (1) the acrylic systems have fast set-up times, and in fact, the set-up times can be varied over very wide limits; (2) various desirable properties can be built into the acrylic systems by incorporation of suitable comonomers into the polymer and monomer-polymer mixture; (3) the acrylic systems are easy to mix and apply and can be made to have relatively long shelf-lives; (4) acrylic systems have been used in restorative materials; (5) most polymers based on methyl methacrylate show very low oral toxicity.

TABLE I  
Acrylic Polymers and Copolymers Utilized in Adhesive Systems

Polymer no.	Nominal composition <sup>a</sup>	Solvent	Isolation method <sup>b</sup>	Yield, %	$[\eta]$ , dl./g. <sup>c</sup>	$\bar{M}_n \times 10^{-3}$ <sup>d</sup>	CTA <sup>e</sup>	Moles, monomer, moles CTA <sup>f</sup>	AIBN, wt.-% on total monomer	Heating time, hr. <sup>g</sup>
1	100% MMA	Benzene	P	49.6	0.0535	9.55	C	57.5	0.200	46
2	100% MMA	Benzene	P	N.D. <sup>h</sup>	—	20	C	214	0.107	70
3	100% MMA	Benzene	FD	N.D.	0.142	32	D	57.8	0.177	144
4	100% MMA	Benzene	P	78.6	0.346	140	D	740	0.094 <sup>i</sup>	144
5	100% MMA	Benzene	P	36.8	0.92	590	None	—	0.0046 <sup>i</sup>	116
6	10% AA	MeOH	W	77.7	—	10	C	57.5	0.207	70
7	20% AA	MeOH	W	85.2	—	10	C	57.5	0.180	118
8	30% AA	MeOH	W	55.4	—	10	C	57.5	0.233	28.5
9	10% AA	—	—	—	—	20	—	—	—	—
10	20% AA	—	—	—	—	20	—	—	—	—
11	30% AA	—	—	—	—	20	—	—	—	—
12	10% MAA	MeOH	W	87.1	ca. 0.05	10	C	57.5	0.200	74
13	20% MAA	MeOH	W	74.8	0.0584	10	C	57.5	0.203	39
14	30% MAA	MeOH	W	47.8	0.074	10	C	57.5	0.273	51
15	10% MAA	EtOH	W	45.7	—	20	A	230	0.107	44
16	20% MAA	EtOH	W	60.8	—	20	A	230	0.123	43.5
17	30% MAA	MeOH	W	N.D.	—	20	A	247	0.194	48
18	10% MA	Benzene	P	N.D.	0.0547	9.75	C	60.3	0.201	68
			FD		0.0575	10.6 <sup>k</sup>				
19	20% MA	Benzene	FD	N.D.	—	10	C	50.7	0.210	47
20	30% MA	Benzene	FD	N.D.	—	10	C	57.5	0.157	90.5

21	40% MA	Benzene	FD	83.5	—	10	C	57.5	0.144	237
22	10% EA	Benzene	FD	20.5	—	10	C	51.5	0.167 <sup>l</sup>	147.5
23	20% EA	Benzene	FD	63.0	—	10	C	57.5	0.148 <sup>m</sup>	187
24	30% EA	Benzene	FD	55.9	—	10	C	27.6	0.314	187
25	10% HFBA	Benzene	P	45.8	—	10	C	57.5	0.168	48
26	20% HEBA	Benzene	P	9.3	—	10	C	57.5	0.176	45
27	30% MEMA	Benzene	P	77.8	—	10	C	57.5	0.177	52
28	10% LMA	Benzene	W <sup>a</sup>	66.6	—	10	C	57.5	0.131	93
29	10% DMAA	Benzene	P	50.2	—	10	C	57.5	0.186	71
30	20% DMAA	Benzene	P	12.9	—	10	C	57.5	0.202	48

<sup>a</sup> Compositions are approximate and are based on mole percentages. With the copolymers listed the other monomer is methyl methacrylate, MMA = methyl methacrylate; AA = acrylic acid; MAA = methacrylic acid; MA = methyl acrylate; EA = ethyl acrylate; HFBA = heptafluoro-*n*-butyl acrylate; NEMA = 2-methoxyethyl methacrylate; LMA = *n*-lauryl methacrylate; DMMA = *N,N*-dimethylacrylamide.

<sup>b</sup> P = precipitation in petroleum ether (b.p. = 30–60°C.); W = precipitation in water; FD = freeze-dried from benzene.

<sup>c</sup> In reagent grade acetone at 25°C.

<sup>d</sup> Viscosity-average molecular weight estimated from viscosity measurements or from the ratio of monomer to chain transfer agent utilized. The latter is a crude approximation. The molecular weight versus intrinsic viscosity relationship of Chinnai and co-workers is used.<sup>4</sup>

<sup>e</sup> Chain transfer agents: A = mercaptoacetic acid; C = mercaptoethanol; D = bromotrichloromethane.

<sup>f</sup> Mole ratio of monomer charged to the chain transfer agent charged.

<sup>g</sup> All polymerizations were carried out at 60 ± 2°C. with mechanical stirring.

<sup>h</sup> Not determined.

<sup>i</sup> 0.0494% additional added after 20 hr.

<sup>j</sup> 0.0020% and 0.0022% additional added after 25 and 68 hr., respectively.

<sup>k</sup> Freeze-dried sample has a number-average molecular weight of 6200 determined on a vapor pressure osmometer.

<sup>l</sup> 0.11% additional added after 26 hr.

<sup>m</sup> 0.079% additional added after 21 hr.

<sup>n</sup> Benzene was evaporated *in vacuo*. Polymer was dissolved in acetone and precipitated in water.

### ACRYLIC ADHESIVE SYSTEMS

Table I lists the various polymers and copolymers that we have utilized in this study. The details of their preparation are listed in the Experimental section.

The adhesives were prepared by dissolving sufficient polymer or copolymer in a monomer mixture (usually identical to the polymer composition) to give a solution of workable viscosity. A known amount of benzoyl peroxide (usually 0.5–1.6 wt.-%) was dissolved in this mixture. When the system was to be used, a known amount of *N,N*-dimethylaniline accelerator was added to the mixture with stirring. The set-up time could be changed by varying both the benzoyl peroxide and *N,N*-dimethylaniline concentrations.<sup>5</sup> An alternative procedure which was sometimes utilized involved dissolving the *N,N*-dimethylaniline in the monomer and mixing the benzoyl peroxide with the polymer. The solid and liquid portions were then mixed rapidly before use. One disadvantage of the latter method is that set-up occurs in many cases before the polymer is completely dissolved.

The polymers utilized were generally of low molecular weight (Table I), i.e., approximately 10,000 or 20,000. Acrylic monomers exhibit very high shrinkages in going to polymer (usually about 20%), so that low molecular weight polymers were used to obtain a high solids content to minimize shrinkage during set. Table II gives some estimated shrinkages for various methyl methacrylate–poly(methyl methacrylate) compositions. Reducing shrinkage during set minimizes the formation of voids, i.e., bubbles, and weak boundary layers.<sup>6a</sup> The strength of the adhesive joint is thus reduced by excessive shrinkage.

TABLE II  
Estimated Shrinkage in Methyl Methacrylate–Poly(methyl Methacrylate)  
Mixtures During Set-Up\*

Viscosity-average molecular weight of polymer additive	Polymer additive in adhesive, wt.-%	Shrinkage of adhesive during set-up, %
$9.4 \times 10^3$	54.8	9.3
$2.0 \times 10^4$	40.0	12.4
$1.4 \times 10^5$	23.8	15.7
$2.0 \times 10^5$	19.7	16.6
—	0.0	20.6

\* Shrinkage was calculated for the reported density for monomer (0.944 g./ml. at 25°C.)<sup>6</sup> and polymer (1.188 g./ml.)<sup>7</sup> assuming no volume change upon mixing and no change of polymer density with molecular weight. The reported shrinkage for methyl methacrylate is 20.6%.<sup>8</sup>

### TESTING PROCEDURE

In order to evaluate the adhesives utilized a test method was developed which allowed many adhesives to be screened.<sup>1</sup> We have broken over

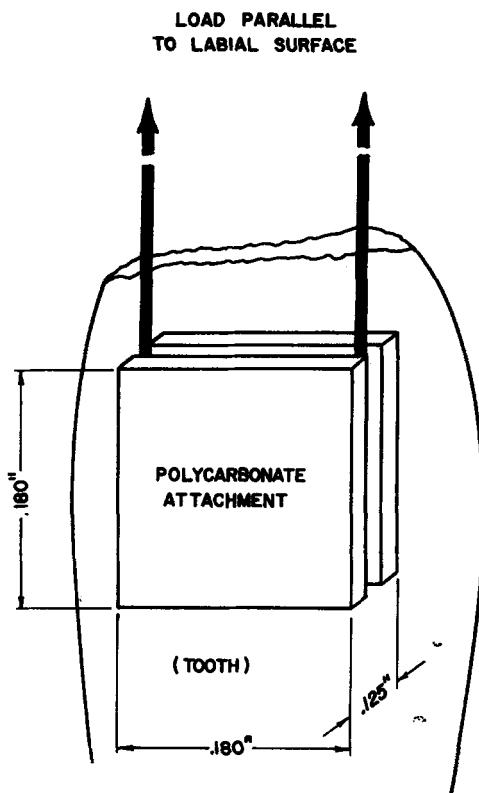


Fig. 1. Testing procedure.

1000 bonds to date. Although our testing method is less complex than some procedures described in the literature,<sup>10-14</sup> it has been sufficient to allow us to differentiate between adhesives. In addition, it more closely duplicates the conditions which would be encountered in practical use of these systems.

We used square polycarbonate (Lexan) attachments grooved to accept the loading wire (Fig. 1). These attachments were bonded to the labial surfaces of the teeth (Fig. 2). The tooth surfaces were treated before bonding with phosphoric acid to increase wettability of the surface toward the adhesive. The bonded specimens were immersed in distilled water at body temperature (37°C.) for 30 days or as described.

A modified shear test was then performed on the samples. This test produces predominantly shear loading but in addition, slight cleavage stresses are also applied (Fig. 2). The stress was increased at a constant rate until bond failure occurred.

The majority of the tests performed to date were with 30-day water immersion, although we have also carried out some time-load tests.

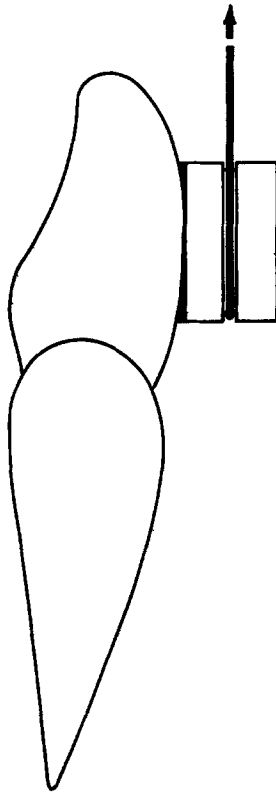


Fig. 2. Testing procedure.

### SURFACE WETTING BY THE ADHESIVE

One important problem which arises in applying the adhesive to tooth surfaces is that of surface wetting. Thus if the adhesive does not properly wet the surface of the adherend, weak boundary layers and voids may be formed which will lower the breaking strength of the adhesive joint.<sup>9b</sup> Very few data are available on the wettability of tooth surfaces. Tooth enamel consists mainly of calcium-deficient hydroxyapatite.<sup>15</sup> Powdered tooth enamel has been shown to be hydrophilic (wetted by water) and hence to have a high energy surface.<sup>25</sup> On the other hand, Newman and Sharpe have carried out contact angle measurements on human tooth surfaces and found that they are hydrophobic.<sup>16</sup> Contact angles in excess of  $50^\circ$  were found for water and angles of about  $35^\circ$  were found for epoxy resins (based on epichlorohydrin and bisphenol A), on pumiced teeth. In addition, it was found that these surfaces could be made hydrophilic by treating with 85% phosphoric acid. Teeth so treated showed essentially zero contact angles with both water and epoxy resins. The tooth surfaces could be restored to their original hydrophobic condition by simply brushing with dental pumice. Measured contact angles returned to their

original high values. These results suggest that enamel is not extensively exposed on the tooth surface and that the surface may be covered with organic material of low surface energy.

We have measured contact angles of the methyl methacrylate-poly-(methyl methacrylate) adhesive system (without added benzoyl peroxide and *N,N*-dimethylaniline) before and after treatment of the tooth surfaces with 40% phosphoric acid. The contact angles had to be measured in an  $N_2$  atmosphere saturated with methyl methacrylate vapor to prevent evaporation of the monomer from the liquid drop. The results are shown in Table III. Clearly the treatment with phosphoric acid lowers the

TABLE III  
Contact Angles of Methyl Methacrylate Adhesives on Tooth Surfaces  
With and Without Phosphoric Acid Treatment\*

Molecular weight of polymer additive	Monomer in adhesive, %	Average contact angle <sup>a</sup>	
		Without treatment	With treatment
$9.4 \times 10^3$	45.2	94°	42°
$2.0 \times 10^4$	60.0	84°	37°
$1.4 \times 10^5$	76.2	69°	34°
$5.9 \times 10^5$	80.3	60°	34°

\* Tooth surfaces treated with 40% phosphoric acid for 1 min., rinsed with distilled water, and dried with cellulose tissue. The untreated samples were pumiced (dental pumice), rinsed with distilled water, and dried with cellulose tissue. The measured contact angles are probably good to  $\pm 5^\circ$ .

observed contact angles quite drastically. On the untreated surfaces the contact angle rises steadily as the amount of polymer in the mix is increased. This is to be expected, since the surface tension  $\gamma$  of methyl methacrylate monomer (28–29 dyne/cm. at 20°C.)<sup>17</sup> is considerably lower than the critical surface tension of wetting for poly(methyl methacrylate) ( $\gamma_c = 39$  dyne/cm. at 20°C.).<sup>18</sup> After phosphoric acid treatment, the contact angles are practically the same within experimental error, suggesting that there is little difference in the surface wetting ability among the four adhesive systems tested. We have demonstrated that the phosphoric acid treatment does improve bond strengths by a large factor in a closely related adhesive system. Thus with a 40% solution of polymer 9 (Table I) dissolved in 10% acrylic acid–90% methyl methacrylate monomer mixture (initiated with benzoyl peroxide and accelerated with *N,N*-dimethylaniline), average modified shear strengths of 61.4 and 710 psi, respectively, were obtained on untreated and treated specimens. The specimens had been immersed in 37° C. water (body temperature) for 30 days prior to breaking the bonds. Clearly surface wetting is thus demonstrated to be an important factor.

The effect of phosphoric acid on increasing the wettability of the tooth surface does not appear to be specific to this acid, since teeth treated in a

similar fashion with 9% hydrochloric acid also show improved adhesion. The molarity of the HCl is about half that of the  $H_3PO_4$  in the above solutions.

### EFFECT OF SHRINKAGE ON BOND STRENGTH

Early in our research we decided to use low molecular weight polymer additives in our adhesive systems specifically to reduce shrinkage during set to fairly low values (Table II). It was decided to standardize on molecular weights of approximately 10,000. The results of bond strength tests on many of these low molecular weight adhesives are presented in Table IV.

TABLE IV  
Bond Strength Tests of Various Low Molecular  
Weight Adhesive Systems

Polymer no. <sup>a</sup>	Molecular weight of polymer additive <sup>b</sup>	Average breaking load, lb. <sup>c</sup>	Average shear stress, psi	Standard deviation, psi
1	10,000	9.6	299	101
2	20,000	25.4	783	249
6	10,000	4.3	133	77
7	10,000	5.6	173	79
8	10,000	9.4	290	107
9	20,000	30.6	944	288
10	20,000	24.4	754	318
11	20,000	17.6	544	92
12	10,000	10.0	309	156
13	10,000	13.0	401	162
14	10,000	13.9	431	189
15	20,000	21.9	676	348
16	20,000	26.0	804	331
17	20,000	29.4	907	531
18	10,000	7.4	230	61
19	10,000	3.1	96.6	53.2
20	10,000	2.1	65.3	34.0
21	10,000	2.5	76	28
22	10,000	6.2	191	56
23	10,000	8.9	275	67
24	10,000	7.6	236	212
25	10,000	4.6	141	66
26	10,000	2.2	68	39
27	10,000	9.1	282	58
28	10,000	4.2	131	45
29	10,000	5.3	162	66
30	10,000	6.5	200	72

<sup>a</sup> Refer to Table I for composition.

<sup>b</sup> Estimated from viscosity measurements or from the amount of chain transfer agent utilized.

<sup>c</sup> Adhesive bonds formed and broken as described in Experimental section. Values represent those obtained from 8-10 specimens after immersion in water for 30 days at 37°C.



TABLE V  
Bond Strength Tests of Methyl Methacrylate Adhesives as a Function  
of Molecular Weight of the Polymer Additive<sup>a</sup>

Molecular weight of polymer additive	Shrinkage during set, %	Average shear strength at bond failure, psi
$9.4 \times 10^4$	8.4	210
$2.0 \times 10^4$	12.0	710
$1.4 \times 10^5$	15.2	430
$5.9 \times 10^5$	18.0	105

<sup>a</sup> Specimens were immersed in 37°C. water for 30 days prior to testing. The average shear strength is for 8-10 specimens at each molecular weight level.

The data in this table show striking improvements in bond strength in going from 10,000 to 20,000 molecular weight polymer additives, even though shrinkage during set was greater in the adhesives of higher molecular weight. This anomalous result prompted us to carry out additional bonding experiments utilizing methyl methacrylate-poly(methyl methacrylate) adhesive systems in which we varied the molecular weight of the polymer additives. These experiments were carried out with 30-day water immersion and with no water immersion. The test results are shown in Tables V and VI. In both test series maxima in bond strength occur with the 20,000 molecular weight polymer additives. The lower molecular weight samples again show poorer bond strengths, and hence these results agree with our observations in Table IV. Although water immersion tends to reduce the bond strengths by about 30% for the 9,400 and 20,000 molecular weight samples the relative order of bond strengths is still the same. The most likely explanation for this anomaly would appear to lie in the physical property differences in the set adhesives. Physical properties, i.e., tensile and shear strengths, are known to be a function of molecular weight, particularly at the low molecular weight end of the scale (typically at number-average molecular weights between 20,000 and 50,000<sup>19</sup> where these properties drop off rather sharply as the molecular weight decreases. We measured the molecular weight of the set adhesives which were utilized for the tests, and these results are shown in Table VII.

TABLE VI  
Bond Strengths of Methyl Methacrylate  
Adhesives Under Dry Conditions<sup>a</sup>

Molecular weight of polymer additive	Shrinkage during set, %	Average shear strength at bond failure, psi
$9.4 \times 10^3$	8.4	383
$2.0 \times 10^4$	12.0	1010
$1.4 \times 10^5$	15.2	680
$2.0 \times 10^5$	16.1	795
$5.9 \times 10^5$	18.0	420

<sup>a</sup> Adhesive bonds were formed and broken as described in the Experimental section. Specimens were stored in dry stoppered test tubes at 37°C. for 24-48 hr. before testing.

TABLE VII  
Molecular Weights of Set-Up Methyl Methacrylate Adhesives<sup>a</sup>

Molecular weight of polymer additive	Molecular weight of set adhesive <sup>b</sup>	Benzoyl peroxide, %	Set-up time, min.
$9.4 \times 10^3$	$3.4 \times 10^4$	0.86	9-11
$2.0 \times 10^4$	$8.7 \times 10^4$	1.3	9-11
$1.4 \times 10^5$	$1.7 \times 10^5$	1.6	10-12
$2.0 \times 10^5$	$1.7 \times 10^5$	1.6	10-12

<sup>a</sup> 1.2% of *N,N*-dimethylaniline was used in all cases.

<sup>b</sup> Determined from intrinsic viscosity measurements and the relationship of Chinai and co-workers.<sup>4</sup>

Clearly the molecular weight is quite low on the set adhesive prepared from the 9,400 molecular weight polymer. An additional observation which tends to support our argument is that failure of the bonds appeared to occur in the bulk adhesive with the lowest molecular weight samples (considerable amounts of adhesive remained on the tooth surface), whereas the breaks usually occurred at or close to the tooth surface-adhesive interface with the higher molecular weight materials.

For the 20,000 and higher molecular weight materials, shrinkage of the adhesive appears to play a predominant role, and the 20,000 molecular weight material offers the best compromise between a final set adhesive which has good physical properties and minimal shrinkage during set-up.

Another method for decreasing shrinkage in the adhesive during set utilizes added powdered inert fillers, i.e., fused quartz.<sup>9c</sup> These fillers may be used with or without added coupling agents.<sup>20, 21</sup> Table VIII shows some results we obtained with added fillers and coupling agents. Added

TABLE VIII  
Effect of Added Fillers on the Bond Strengths of Methyl Methacrylate Adhesives<sup>a</sup>

Filler	Average breaking load, lb.	Average shear stress, psi	Standard deviation, psi
Base filler <sup>b</sup>	28.5	880	262
Base filler + quartz <sup>c</sup>	32.5	1005	248
Base filler + quartz + coupling agent <sup>d</sup>	29.9	923	199
Base filler + coupling agent <sup>e</sup>	24.3	750	321

<sup>a</sup> Teeth were pretreated with phosphoric acid, and bonded specimens were immersed in 37°C. distilled water for 30 days. See Experimental section for details. Set-up time was about 15 min.

<sup>b</sup> Base filler: 40 parts polymer (20,000 M.W.), 60 parts monomer, 1% benzoyl peroxide, 2% *N,N*-dimethylaniline.

<sup>c</sup> Same mix as base filler with 28% added fused quartz (General Electric Company).

<sup>d</sup> Same mix as base filler with 28% added fused quartz (General Electric Company) and 1.9% Dow Corning Z-6030 coupling agent (a methacrylate functional silane).

<sup>e</sup> Same mix as base filler with 2.4% Dow Corning Z-6030 coupling agent (a methacrylate-functional silane).

quartz improved the bond strengths by about 12%, whereas quartz and coupling agent (a methacrylate-functional silane) showed only a 4.5% improvement. The standard deviation in the latter system was considerably better, however, and this may indicate a higher reliability for this adhesive. Obviously, more tests should be conducted to establish this point. The added Z-6030 coupling agent appeared to decrease average stress and increase the standard deviation. Our data are not sufficient to allow any conclusion to be drawn about the relative effectiveness of the two methods we used for increasing bond strength via reducing shrinkage during set. Further investigation of this point would be highly desirable.

### EFFECT OF WATER IMMERSION ON BOND STRENGTH

It is clear from the data in Tables V and VI that water immersion of the specimens for 30 days does decrease bond strengths. Thus for the four common molecular weights listed in the two tables the decrease in bond strengths amounts to 45, 30, 37, and 75%, respectively, in order of increasing molecular weight. The strongest joints show the smallest per cent decrease.

We have conducted preliminary experiments to determine the rate of breakdown with time. These results are shown in Figure 3. The effect of water degradation becomes apparent 1-3 hr. after bonding with specimens immersed in 37°C. water. The loss in strength appears to be proportional to the logarithm of time after the peak strength has been attained. The lines obtained in Figure 3 (after the peak) represent a

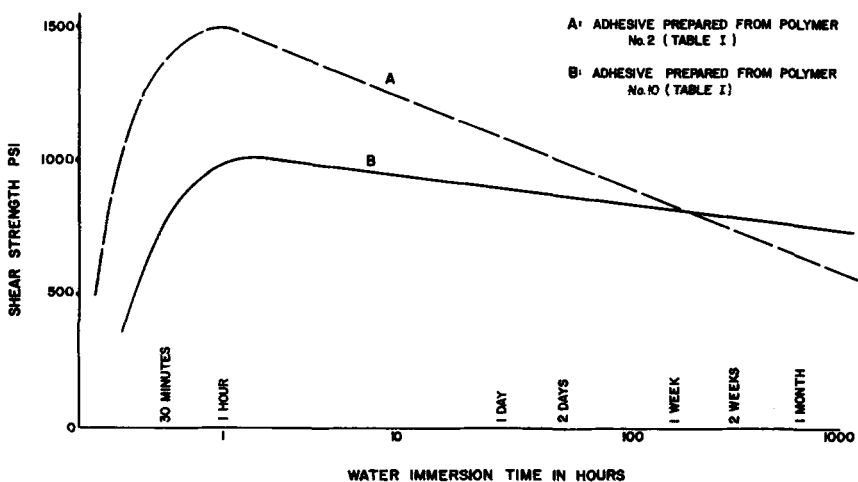


Fig. 3. Nominal shear strength (load/area) vs. log time: (A) adhesive prepared from polymer 2 (Table I); (B) adhesive prepared from polymer 10 (Table I).

least-squares fit of data points up to 6 weeks immersion time. If these lines are extrapolated to 6 months and 1 year, the average strengths predicted are 410 and 290 psi, respectively, for the methyl methacrylate; 690 and 650 psi, respectively, for the 80/20 copolymer of methyl methacrylate-methacrylic acid. Both adhesives are thus able to form joints with some degree of permanency. The methyl methacrylate system appears to break down more rapidly, although its rate is still reasonably slow.

### RELIABILITY OF THE ADHESIVE SYSTEMS STUDIED

One of the biggest problems in the present study is to find adhesives which show high average shear strengths with relatively small standard deviations. We have selected the average shear strength less three standard deviations as a criterion of reliability.<sup>22,23</sup> With a normally distributed population, only 0.135% of these shear strengths should fall below the  $\bar{x} - 3\sigma$  level. Thus we may be 99.865% sure of our sample when this load is not exceeded. Our results for six copolymers and three methyl methacrylate systems are shown in Figure 4. All specimens were immersed in 37° C. water for 30 days prior to testing. Molecular weights of all the polymer additives were approximately 20,000.

Only one of the adhesives showed no residual strength for the  $\bar{x} - 3\sigma$  limit. The 30% methacrylic acid copolymer showed quite high reliability, with expectations that 99.865% of the specimens would have shear strengths equal to or better than 470 psi. These results together with the

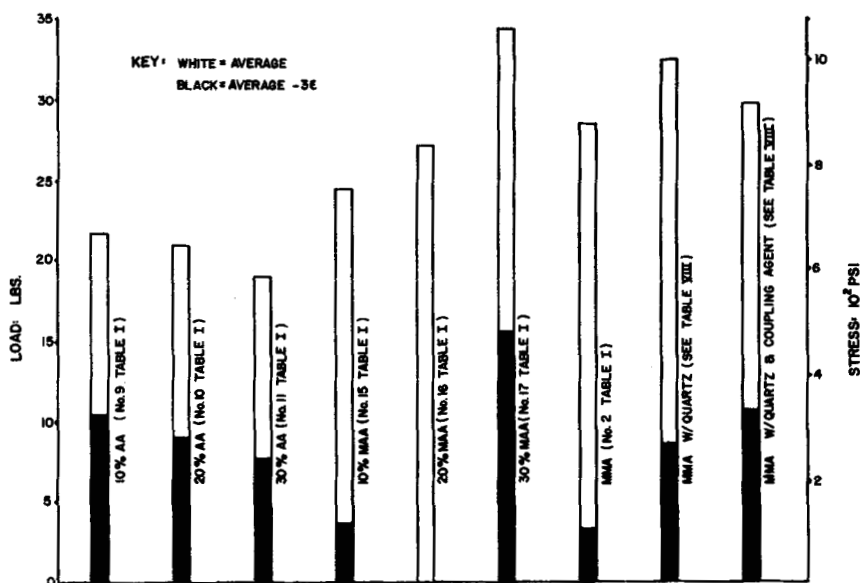


Fig. 4. Results of 30-day immersion tests: (white bar) average; (black bar) average— $3\sigma$ .

time-load tests reported in the previous section lead us to believe that a successful fast-setting acrylic system can be developed with the necessary reliability for bonding to tooth surfaces.

## EXPERIMENTAL

### Preparation of Polymers and Copolymers

All monomers, chain transfer agents, and solvents were obtained commercially and were generally reagent grade materials. (Distillation Products, Fisher Scientific and Monomer-Polymer Laboratories.) The azobisisobutyronitrile (AIBN) was obtained from the Du Pont Company. Inhibitors were removed from the monomers by vacuum distillation prior to polymerization.

Polymerizations were carried out in a glass resin kettle fitted with mechanical stirrer and reflux condenser. The resin kettle was immersed in a constant temperature bath maintained at  $60 \pm 2^\circ\text{C}$ . Generally 50-100 g. of monomer (or monomer mixture) was charged into about 150 ml. of solvent. The temperature was raised only after the system was purged with nitrogen and the slow nitrogen purge was maintained throughout the polymerization. After the polymerization was complete, polymer was recovered by precipitation in a large excess of nonsolvent (See Table I) or freeze-dried from benzene solution. The precipitated polymers were dried in a vacuum oven at about  $50^\circ\text{C}$ . Table I gives the important details on polymer and copolymer preparation.

### Preparation of Adhesives

Adhesives were prepared by dissolving a given amount of polymer (copolymer) in a weighed amount of monomer (monomer mixture) of the same composition. A weighed amount of benzoyl peroxide was then dissolved in this viscous mixture. When the adhesive was to be used, a given amount of *N,N*-dimethylaniline (DMA) was added with a micro dropper. Table IX shows the composition of adhesives when various molecular weight polymer (copolymer) additives were employed. Set-up times of 10-15 min. were desirable in bonding experiments. Slow set-up times (30-45 min.) tended to give poor bond strengths since specimens were immersed in water before the adhesive was completely set (see below).

The adhesives were prepared with inhibited monomers used as received. Mixing of the components was accomplished with small wooden splints. The compositions shown in Table IX gave solutions of workable viscosity.

### Preparation of Teeth and Plastic Attachments

The teeth employed were recently extracted upper central incisors, cleaned of debris with dental pumice and stored in room temperature tap water. The roots of the incisors were notched and imbedded in copper lugs with fast-setting acrylic adhesive. Placement in lugs facilitated the shear strength test described below.

TABLE IX  
Composition of Adhesives Employing Polymer  
or Copolymer Additives\*

Nominal molecular weight of polymer additive	Polymer in adhesive, %	Benzoyl peroxide, %	DMA* added, %
10,000	60 ± 6	0.5-2.0	1.2-2.0
20,000	40 ± 5	0.5-2.0	1.2-2.0
140,000	25 ± 5	0.5-2.0	1.2-2.0
200,000	20 ± 5	0.5-2.0	1.2-2.0
600,000	10 ± 5	0.5-2.0	1.2-2.0

\* Set-up time varied widely. At the lowest levels of benzoyl peroxide and DMA concentrations shown, set-up time is approximately 45 min.; at the highest levels, approximately 5 min. At 1% benzoyl peroxide and 1.2% DMA levels, set-up time is about 10-15 min. for 2-g. samples.

Test attachments (0.180 in.<sup>2</sup>) were cut from 1/8-in. thick polycarbonate sheet (Lexan) and were grooved on the edges to accept the loading wire (see Figs. 1 and 2).

#### Formation of the Adhesive Bonds by Dry Bonding Procedure

The procedure used for bonding to the teeth used in obtaining the data reported in Table VI is as follows.

The polycarbonate attachments were roughened on one side with fine sand paper, rinsed in *n*-hexane, and air-dried.

The teeth (embedded in lugs) were pumiced (dental pumice), rinsed, and left in tap water overnight. The teeth were then removed from the water and wiped dry with cellulose tissue. The tooth surfaces were treated with 40% phosphoric acid for 60 sec., then were immediately rinsed thoroughly with tap water and finally wiped dry with cellulose tissue.

The monomer-polymer mixtures were made up previously to correspond to the shrinkages listed in Table VI and contained 1% benzoyl peroxide; 1.2% DMA was added to 1 g. of mix.

The adhesive was applied to the tooth surface and roughened attachments surface with a small wooden splint. The attachment was pressed onto the tooth surface with light finger pressure.

The bonded specimens were allowed to stand in air at room temperature for 30 min. and were then placed in dry test tubes which were stoppered and placed in a 37°C. constant temperature bath.

The specimens were tested 24-48 hr. after bonding by the procedure described below. Each reported shear strength is the average for 8-10 specimens.

#### Adhesive Bonding for 30-Day Immersion Tests

The bonding procedure in these tests was similar to the above procedure except for the following changes:

The pumiced teeth were immediately treated with 40%  $H_3PO_4$  for 60 sec., rinsed with tap water, and wiped dry. The bonded specimens were placed in test tubes containing tap water, and the stoppered tubes were then placed in 37°C. constant temperature bath for 30 days.

It was found that teeth could be used over and over again for many bonding experiments provided that the old adhesive was thoroughly removed by scraping and the surface was then pumiced. The original hydrophobic condition of the tooth surface is restored by pumicing.<sup>16</sup> We also have not observed any harmful effects of repeated 60-sec. 40% phosphoric acid treatments on the tooth surfaces as viewed under a low power microscope. Fresh teeth give similar bond strengths compared to reused teeth when bonded under similar conditions with the same adhesive.

### Testing of Specimens and Estimation of Shear Strengths

A Chatillon Model DTC universal tester was utilized for all shear strength tests. The copper lugs holding the specimens were clamped firmly in the vise of the test apparatus (Fig. 5). The loading wire was fitted in the groove of the plastic attachment and attached to the hook on the testing apparatus so that the applied load was closely parallel to the adhesive joint (Figs. 1, 2, and 5). The load was then applied at the rate of 1 lb./sec. until joint failure occurred. The shear stress was then obtained by dividing the breaking load by the attachment area (0.0324 in.<sup>2</sup>).

During adhesive bonding there is some overrun of the liquid adhesive, so that area of the set adhesive in contact with the tooth surface is somewhat larger than the attachment area (in some cases as high as 0.07 in.<sup>2</sup>). However, when an attempt was made to correlate this overrun area with breaking strength no correlation was found. This is not too surprising in view of the fairly large standard deviations in breaking loads that we observe. These large deviations result from the operation of other possibly more important variables which are difficult to control in our test; i.e., surface roughness, surface curvature, organic debris on the tooth surface, thickness of the adhesive layer, etc.

### Measurement of Contact Angles

A 1000-ml. beaker was inverted on a lab jack. Methyl methacrylate was placed in a column partially filled with beryl saddles. The column was fitted with a nitrogen inlet tube and gas outlet tube which led directly into the closure provided by the beaker through a hole in the lab jack surface. This hole and the column were fitted with rubber stoppers. A gas outlet tube was also fitted to a second hole on the jack surface with a rubber stopper. A good seal between the beaker and jack surface was obtained with modeling clay. The closure thus constructed could be slowly purged with nitrogen saturated with methyl methacrylate vapor to prevent evaporation of monomer from the adhesive solutions used in the contact angle measurements.



Fig. 5. Loading of adhesive joint.

The recently extracted upper central incisors used were imbedded in modeling clay so that the labial surfaces were up and horizontal on the jack surface inside the closure. Adhesive was introduced onto the tooth surface with a dissecting needle. Contact angle measurements were made with a Gaertner contact angle goniometer (Gaertner Scientific Corporation, Chicago, Illinois). The angles observed became constant after 5-6 min. The angles observed at room temperature are shown in Table III. The teeth were treated immediately before the measurements were made as indicated in Table III.

### CONCLUSIONS

It is apparent from the previous discussion that improved adhesion to tooth surfaces may be obtained by pretreatment of these surfaces with mineral acids. The acid treatment raises the critical surface tension of



wetting to a point where it more closely matches the surface tension of the adhesive.

Another important factor is to reduce shrinkage of the adhesive during set to as low a level as possible without so reducing the physical properties of the set adhesive so that the bond strength is also impaired. We have found that the optimum molecular weight for the polymer additives utilized in the fast-setting acrylic system is around 20,000. Thus a 40% polymer solution in 60% monomer gives an adhesive of acceptable viscosity and 12.4% shrinkage during set. Use of lower molecular weight gives set adhesives with poor physical properties.

Further improvement in joint strength is noted when powdered fused quartz is added to the adhesive as filler. If a silane coupling agent is added along with the quartz no significant improvement in joint strength is noted. Coupling agent without the added quartz actually decreased joint strength substantially.

Water immersion at 37°C. reduces joint strengths substantially with time. However, the effect is not nearly as large as reported previously.<sup>10,24</sup> Some of our test results suggest that breakdown of the adhesive joints by water is less significant for the stronger adhesive bonds. The breakdown appears to be proportional to the logarithm of the time after peak strength has been attained.

We conclude on the basis of the present study that reliable, fast-setting acrylic adhesive systems are attainable and that further investigation will produce a practical system which will have value in orthodontics and restorative dentistry.

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### Résumé

Certains des problèmes rencontrés dans l'adhésion des substances plastiques à des surfaces de dents humaines ont été étudiés. Des adhésifs acryliques basés sur un mélange du monomère méthacrylate de méthyle et du polyméthacrylate de méthyle avec initiation au peroxyde de benzoyle et du *N,N*-diméthyl-aniline comme accélérateur ont été utilisés. Les homopolymères et copolymères ont été étudiés tous les deux. Des incisives supérieures récemment extraites ont été utilisées pour les expériences d'adhésion. La force de liaison a été améliorée par traitement préalable des surfaces dentaires avec des acides minéraux tels que le  $H_3PO_4$ . Le mouillage de la surface par l'adhésif liquide est amélioré par le traitement acide. Le poids moléculaire du polymère ou du copolymère employé dans l'adhésif liquide exerce un effet important sur la force de la liaison. Le poids moléculaire optimum pour obtenir une force de liaison maximum s'éleve à 20.000 g/mole. L'immersion dans l'eau à 37°C d'échantillons liés pour des périodes allant jusque 6 semaines exerce un effet néfaste sur la force du lien. Néanmoins, on montre que certains des adhésifs forment des liens raisonnablement forts pour des périodes dépassant 6 mois même sous immersion dans l'eau.

### Zusammenfassung

Einige bei der Klebebindung von Plastomeren an menschliche Zahnoberflächen auftretende Probleme wurden untersucht. Acrylklebstoffe auf Grundlage von Polymethylmethacrylat-Methylmethacrylatmonomer-Mischungen mit Initiierung durch Benzoylperoxyd bei *N,N*-Dimethylaminbeschleunigung wurden benützt. Sowohl Homopolymere als auch Copolymere wurden untersucht. Zu den Klebeversuchen wurden frisch gezogene obere mittlere Schneidezähne verwendet. Die Klebefestigkeit wurde durch Vorbehandlung der Zahnoberfläche mit Mineralsäuren wie  $H_3PO_4$  verbessert. Es zeigte sich, dass die Oberflächenbenetzung durch den flüssigen Klebstoff durch die Säurebehandlung verbessert wird. Das Molekulargewicht des im flüssigen Klebstoff verwendeten Polymeren oder Copolymeren besass grossen Einfluss auf die Klebefestigkeit. Das optimale Molekulargewicht für die Erzielung einer maximalen Bindungsfestigkeit lag um 20.000. Eine Immersion der verklebten Proben in Wasser bei 37°C für

Dauern bis zu sechs Wochen hatte einen ungünstigen Einfluss auf die Bindungsfestigkeit. Es konnte aber doch gezeigt werden, dass einige Klebstoffe Bindungen von brauchbarer Festigkeit für längere Dauern als sechs Monate sogar bei Wasserimmersion bildeten.

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