Effect of resin application time on bond strength of polymer substrate repaired with particulate filler composite

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Four different polymeric substrates were treated with unfilled intermediate resin (IMR) for various lengths of time (15 s, 3 min, 1 h, 24 h, and 2 weeks) to find out the effect of IMR treating time on shear bond strength between the substrate and a particulate filler composite. The IMR used in the study was a diacrylate monomer resin and the particulate filler composite was added on it. Two of the tested substrates were fiber-reinforced composites (FRCs). Two other substrates were cross-linked bisphenol-A-glycidyl dimethacrylate/triethyleneglycol dimethacrylate (BisGMA/TEGDMA) substrate and linear polymethylmethacrylate substrate. The bond strength of the particulate filler composite to the BisGMA/TEGDMA substrate was significantly higher compared to the other substrates ($p < 0.001$). A correlation between increasing shear bond strength and longer treating time were found with the BisGMA/TEGDMA substrates ($r = 0.594$, $p < 0.001$) whereas no correlation was found with the other substrates. Prolonging of IMR treating time enhanced the BisGMA/TEGDMA substrate bond strength to the particulate filler composite but it had no clear effect on the bond strength of other substrates.

1. Introduction

Several surface treatment methods have been introduced in order to enhance the bond strength between the restorative composite substrate and repair composites. The use of low viscosity unfilled intermediate resin (IMR) significantly improved the bond strength with the bisphenol-A-glycidyl dimethacrylate (BisGMA) substrate while IMR with urethane-based particulate filler composite resin substrate did not enhance the bond strength [1]. Chalkey *et al.* [2] supposed that the unfilled IMR was a better wetting agent than the particulate filler composite. The results by Kallio *et al.* [3] suggested that high shear bond strengths were related to specific polymer/composite and IMR materials. That study also revealed that in most of the cases IMR improved the bond strength but in some cases, especially with flow viscosity particulate filler composites the adhesion properties were better without the IMR. Some of the previous studies have shown that better bond strengths can be achieved with phosphonate ester bonding resins than with the unfilled IMRs when repairing composite resins [4–6].

The bond between the polymer substrate and new composite can be formed by two different ways. The presence of unreacted pendant functional groups with carbon–carbon double bonds in the polymer chains on the surface of the polymer substrate can allow free radical polymerization between the substrate and the new composite resin. Previous studies have shown that composite repairs of particulate filler composite with dimethacrylate polymer matrix generally have bond strengths of 20% up to 70% of the cohesive strength of bulk materials [4, 6–11]. The greatest reactivity of the substrate to the formation of covalent bonding can be found on the surface during the first 24 h after polymerization of the substrate [12].

Another mechanism to bond the substrate and the new composite resin is based on formation of an interpenetrating polymer network (IPN). The swelling of the linear phases of the substrate by monomer diffusion, i.e. by ''monomer resin solvent'' allows locking of the newly formed polymer chains into the swelled substrate surface. The swelling can be obtained especially with linear polymers, whereas cross-linked polymers are more difficult to swell. The depth of the IPN-layer between the acrylic resin polymer teeth and polymethyl methacrylate (PMMA) based on multiphase denture base polymers has been studied by Vallittu and Ruyter [13]. Monomer penetration into the denture base polymer and into the acrylic resin teeth was promoted by increasing the polymerization temperature. Other factors influencing the penetration are time and type of monomeric solvent.

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The use of fiber-reinforced composite (FRC) appliances is increasing at the moment. The polymer-preimpregnated fiber-reinforcement has been shown to be useful in eliminating fractures of acrylic resin removable dentures [14]. The use of FRCs in dental appliances such as crown and bridges has allowed more tooth-saving prosthodontic treatment with fixed partial dentures technology [15–19]. It is therefore expected that the repairs or modifications of these FRC applications may become more common in the future. The most common resins that are used with fixed FRC appliances are BisGMA and triethyleneglycol dimethacrylate (TEGDMA). After polymerization, these resins form a cross-linked polymer network. PMMA is commonly used as linear polymer for fiber-reinforced removable complete dentures and partial dentures. Clinically, it is of great importance to know whether application time of adhesive resin on bonding surface of appliance repaired in laboratory has an effect on the bond strength.

Although the use of the unfilled IMR has been investigated [3, 4, 20–22] there is lack of information on effect of the unfilled IMR treating time on bond strength between the new resin and polymer substrate. The purpose of this study was to investigate the effect of the unfilled diacrylate IMR treatment time on two different FRC substrates (filled), PMMA substrate (unfilled) and BisGMA/TEGDMA substrate (unfilled) by determining the bond strength between the IMR treated substrate and a particulate filler composite.

2. Materials and methods

The materials used in this study are listed in Table I. StickNet was a woven fiber product with bi-directional fiber orientation and Stick was a continuous unidirectional fiber product. The fibers were preimpregnated with porous linear PMMA. The FRC substrates were fabricated by incorporating a diacrylate monomer system (Sinfony activator) into the preimpregnated Stick and StickNet fibers. The cross-linked substrate was made of BisGMA/TEGDMA monomer system containing 70% BisGMA, 29.2% TEGDMA, 0.4% camphorquinone initiator and 0.4% 2-dimethylaminoethyl methacrylate (DMAEMA) catalyst by weight. The linear PMMA substrate was made of methylmethacrylate (MMA) monomer. The substrates contained 98.6% MMA, 0.4% benzoyl peroxide polymerization initiator and 0.4% N,N-dimethyl-p-toluidine as the catalyst by weight.

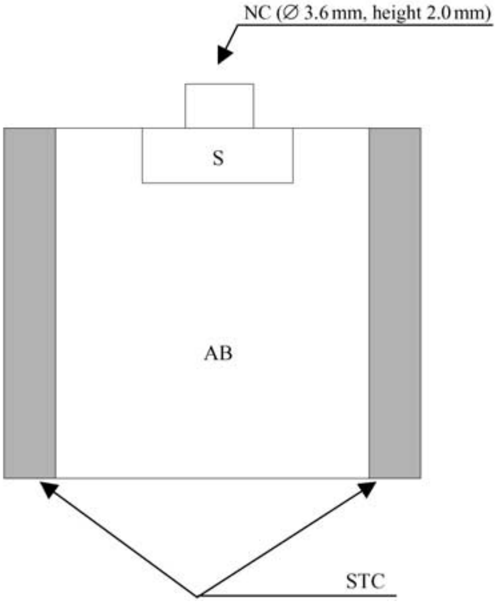

Figure 1 Schematic diagram of test specimen. NC, new composite; S, substrate; AB, acrylic block; STC, stainless steel cylinder.

The substrates were applied to the metal cylinders filled with autopolymerizing denture base polymer (Fig. 1). The unpolymerized substrate material was pressed into the cavity within the acrylic polymer surrounded by the metal cylinder with the help of a transparent mylar sheet. Stick, StickNet and BisGMA/TEGDMA substrates were initially light polymerized with a hand light-curing unit (Elipar, 3M-Espe, Seefeld, Germany) using a wave length of 483 nm for 40 s. Final polymerization was completed in a light curing oven (Liculite, Dentsply, Dreieich, Germany) for 5 min in which the temperature rose up to 85 °C. PMMA substrates were autopolymerized in water at 300 kPa air pressure at 70 °C for 15 min, prior to packing in the substrates.

The substrate surfaces ($n = 100$ in 20 different groups) were wet ground flat with 1200 grit (FEPA) silicon carbide grinding paper. In the case of FRC substrates the fibers were exposed during the grinding. The test

TABLE I Materials used in the study

Code	Description of material	Manufacturer	Lot no.	Type of material
Stick	E-glass and polymethylmethacrylate	StickTech Ltd., Turku, Finland	1980310-R-0041	FRC
StickNet	E-glass and polymethylmethacrylate	StickTech Ltd., Turku, Finland	1990308-W-0035	FRC
BisGMA	Bisphenol-A-glycidyl dimethacrylate	Chemotechnique Diagnostics, Tygelsjö, Sweden	400631	Monomer
TEGDMA	Triethyleneglycol dimethacrylate	Sigma-Aldrich, Steinheim, Germany	07304-067	Monomer
MMA	Methylmethacrylate	Sigma-Aldrich, Steinheim, Germany	398474/1 31899	Monomer
Sinfony dentin D/A4	Octahydro-4,7-methano-1H-indenediyl-bismethylenediacrylate 10–30 wt % + fillers	3M-ESPE Dental-Medizin GmbH & Co., Seefeld, Germany	FW 0052367	Veneering composite
Sinfony activator	Octahydro-4,7-methano-1H-indenediyl-bismethylenediacrylate	3M-ESPE Dental-Medizin GmbH & Co., Seefeld, Germany	FW 0056835	Intermediate resin
DMAEMA	2-dimethylaminoethyl methacrylate	Sigma-Aldrich, Steinheim, Germany	363172/1 43598	Catalyst
	N,N-dimethyl-p-toluidine	Sigma-Aldrich, Steinheim, Germany	23208-058	Catalyst
	Camphorquinone	Fluka Chemie, Buchs, Switzerland	395656/1 399	Initiator
	Benzoylperoxide	Merck, Schuchardt, Germany	5219564	Initiator

FRC, fiber-reinforced composite.

TABLE II The influence of type of substrate and IMR treatment time on shear bond strength values as analyzed by two-way ANOVA

Source	Type III sum of squares	df	Mean Square	F	Sig.
Substrate	7987.713	3	2662.571	119.892	0.001
Time	449.535	4	112.384	5.061	0.001
Substrate × time	1603.757	12	133.646	6.018	0.001

$R^2 = 0.850$ (adjusted $R^2 = 0.814$).

specimens were cleaned in distilled water in an ultra sonic cleaning machine (Quantrex 90, L&R Ultrasonics, NJ) for 15 min. The substrates were stored in a desiccator at room temperature for 48 h. The ground and stored substrate surfaces were treated with an unfilled diacrylate IMR (Sinfony activator, see composition in Table I) either 15 s, 3 min, 60 min, 24 h or 2 weeks. Sinfony activator was a low viscosity, intermediate resin that was part of the dental laboratory veneering composite resin system manufactured by 3M-ESPE. A drop of IMR was applied on each substrate surface from the original bottle of the manufacturer. The IMR was spread on the substrate surface with the help of a composite resin application instrument. After that the specimens were left in a light protected chamber for previously mentioned periods at room temperature. The particulate filler composite resin (Sinfony dentin) was then applied on the substrate surface by using a translucent tubular polyethylene mold with an inner diameter of 3.6 mm. The composite resin was injected into the mold from a syringe and initially polymerized with the hand light-curing unit for 40 s. The polyethylene mold was gently removed from the test specimen and the final polymerization was completed in the light-curing oven (Liculite, Dentsply, Dreieich, Germany) for 5 min.

The test specimens were stored dry at room temperature for 48 h before testing the samples. The specimens were mounted in a jig (Bencor Multi-T shear assembly, Danville Engineering Inc., San Ramon, CA) of the universal testing machine (Lloyd LRX, Lloyd Instruments Ltd, Fareham, UK) and the shear force was applied until fracture occurred. The specimens were loaded at a crosshead speed of 1.0 mm/min and the stress strain curve was analyzed with Nexygen 2.0 software (Lloyd Instruments Ltd, Fareham, UK). The fractured interfaces were visually examined to find out whether the fractures were cohesive or adhesive. The fracture was considered to be cohesive if at least 25% of the interface area was covered with a layer of substrate or a layer of additional composite resin.

To examine the dissolving capability of the substrates by the IMR the treated substrate surfaces were examined with the scanning electron microscope (SEM). Three specimens from each substrate group were wet ground flat with 4000 grit silicon carbide grinding paper. The treatment time was 5 min for the IMR. Topographical changes of the surface were considered as dissolved substrate surface.

The shear bond strengths of all 20 groups were analyzed statistically with analysis of variance (ANOVA) with Dunnett's T3 *post hoc* test with SPSS (Statistical Package for Social Science, SPSS Inc., Chicago, Ill) to establish the effect of substrate type and the effect of IMR treating time on shear bond strength. The mean difference was significant at the level 0.05. Regression analysis was performed to establish the correlation between the IMR treatment times on the shear bond strengths with various substrates.

3. Results

The two-way ANOVA (Table II) revealed significant differences ($p < 0.001$) related to the IMR treatment time and to the type of substrate. The bond strength of BisGMA/TEGDMA substrates was significantly higher compared to the other substrates ($p < 0.001$) (Table III). The difference of shear bond strengths between StickNet and PMMA was significant ($p < 0.001$) (Table III). The difference between Stick and StickNet was slightly significant ($p < 0.049$) and the bond strength of the Stick group was significantly higher compared to the weakest group of PMMA ($p < 0.001$) (Table III).

IMR treatment time showed a medium correlation on shear bond strength with BisGMA/TEGDMA group ($p < 0.001$, $r = 0.594$) (Fig. 2(a)). The second highest shear bond strengths were achieved in the StickNet group

TABLE III Dunnett's T3 multiple comparison between average substrate shear bond strengths

Substrate	Substrate	95% confidence interval		
		$p <$	Lower bound	Upper bound
BisGMA/TEGDMA	StickNet	0.001	8.056	20.752
	Stick	0.001	12.011	24.437
	PMMA	0.001	18.334	30.229
StickNet	BisGMA/TEGDMA	0.001	− 20.752	− 8.056
	Stick	0.049	0.014	7.626
	PMMA	0.001	6.578	13.178
Stick	BisGMA/TEGDMA	0.001	− 24.437	− 12.011
	StickNet	0.049	− 7.626	− 0.014
	PMMA	0.001	3.098	9.017
PMMA	BisGMA/TEGDMA	0.001	− 30.229	− 18.334
	StickNet	0.001	− 13.178	− 6.578
	Stick	0.001	− 9.017	− 3.098

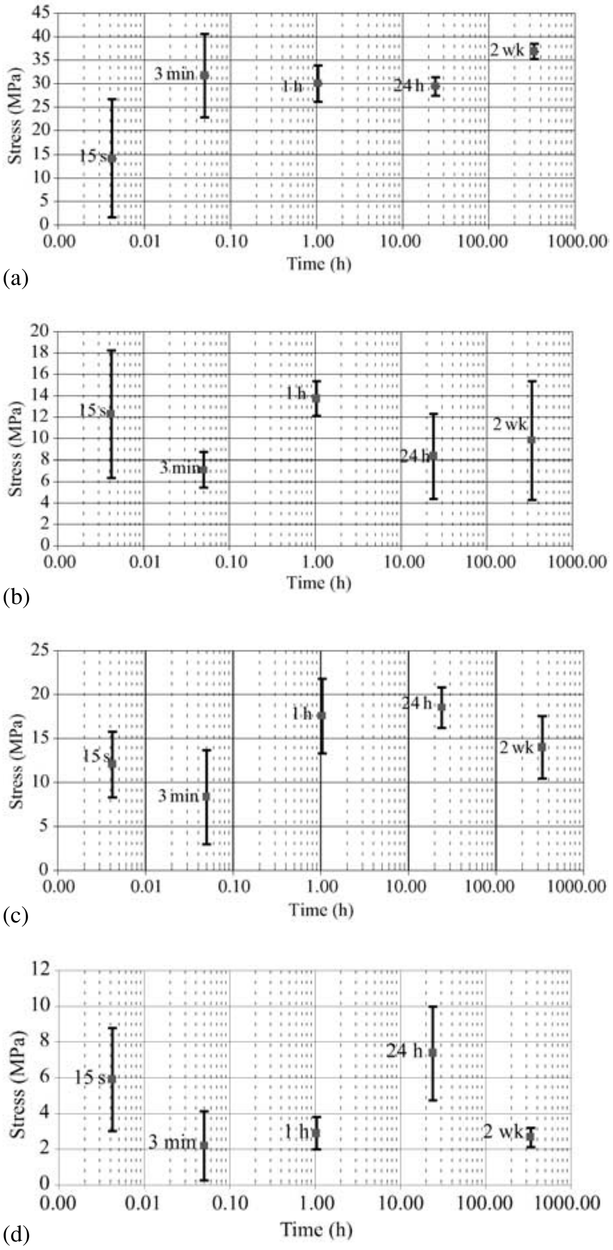

Figure 2 IMR treatment time of the substrate (a) BisGMA/TEGDMA, (b) Stick, (c) StickNet, and (d) PMMA plotted to the shear bond strength values.

in which IMR treatment time correlation on shear bond strength was: $p < 0.023$, $r = 0.403$ (Fig. 2(c)). No correlation for IMR treatment time on shear bond strength was found in the case of PMMA group ($p < 0.428$, $r = -0.038$) (Fig. 2(d)). IMR treatment time did not show correlation on shear bond strength with the Stick group ($p < 0.296$, $r = -0.112$) (Fig. 2(b)).

The examination of fractured interfaces revealed that 96% of the PMMA substrate fractures and 92% of the Stick substrate fractures were adhesional. In the case of StickNet specimens all the fractures were considered as cohesional. Most of the fractures with BisGMA/TEGDMA specimens were cohesive (96%). The test damaged severely the BisGMA/TEGDMA substrate giving an indication of a strong bond between the substrate and the new composite. According to the SEM examination, no evidence of topographical change was found that the IMR would have dissolved the surfaces of different substrates.

4. Discussion

This study demonstrated the shear bond strength between different types of polymer substrates and particulate filler composite after the substrate had been treated with IMR for various lengths of time. The long time span (15 s–2 weeks) was selected for this study to find differences between various substrates. Especially, the longer treatment times are impractical for clinical use by many times but may be used in laboratory-made appliances. The shear bond strength test was chosen, because it is a well-documented testing method in dental materials research [23]. Thermocycling was not performed on the test specimens because the effect of thermocycling on shear bond strength was evaluated in our previous study [3].

Nilsson *et al.* [24] studied the shear bond strength between composite inlay material and resin cement and they found that the untreated (the treated specimens were either ground, sandblasted or sandblasted and silanized) series of composite inlays had higher coefficients of variation compared to the pretreated ones. They concluded that the nature of the bond is likely to be more dependent on the mechanical than chemical basis. No difference has been found between different composites and materials with the same resin formulation concerning the repair bond strength [11, 25], although, it has also been claimed that materials of the same structured family as the original composite resin should be used with repairs in order to achieve the maximum chemical bond strength [26]. However, clinicians have to face the fact that generally the origin of the material and the polymer matrix remains unknown.

The results of our study suggest that the functioning of the diacrylate IMR used in this study might not be ideal for obtaining an interdiffusion bonding based on IPN. It was found that the high shear bond strengths were not dependent on the diacrylate IMR treatment time with PMMA, Stick and StickNet substrates. The time-dependence enhancement in bond strength values could have been explained by the prolonged dissolving time of the IMR on the substrate surface, but because no topographical changes were found by SEM the diffusion based swelling did not happen. The dissolving of the substrate requires the polymer to be soluble which means that the polymer substrate should ideally be linear polymer. In the case of PMMA, the substrate was a linear and in the case of Stick and StickNet the FRC substrate was composed of glass fibers, diacrylate polymer and randomly located isles of linear preimpregnation polymer matrix. The BisGMA/TEGDMA substrate was a cross-linked polymer only. Vallittu *et al.* [27] showed that MMA with small quantity of cross-linking monomer effectively dissolves the surface of denture base polymers. However, this dissolving pattern of the substrate surface was not found with Sinfony activator diacrylate IMR. Concerning the other substrates no evidence was found in the SEM analysis that the IMR would affect the substrate surface.

It is of interest that the results with BisGMA/TEGDMA substrate were different to some extent when compared to the other substrates. The relation between the high shear bond strengths and longer IMR treatment periods could be seen. However, it must be noted that the major improvement was achieved during the first 3 min. Prolonging treatment time up to 2 weeks did not improve the bond strength as much as the first 3 min did. When the IMR treatment time was prolonged, the variation of the results in subgroups was diminished in the BisGMA/TEGDMA group. It can be assumed that the longer IMR treatment times give more reliable and stronger bond strength in the case of the BisGMA/TEGDMA substrate group. The type of bond failure was mainly cohesive but some of the weakest specimens showed partially adhesive failure, especially in the shortest treatment period group.

The IMR might penetrate into the substrate surface irregularity during the longer treating periods. According to SEM images no evidence was found of substrate dissolving caused by the IMR. High shear bond strengths achieved with the BisGMA/TEGDMA substrates were likely to be related to free radical polymerization of unreacted methacrylate groups on the surface. It is known that the chemical bond functions in the case of BisGMA/TEGDMA with a relatively low degree of conversion degree [28]. We can assume that the number of residual free carbon-carbon double bonds is higher on the BisGMA/TEGDMA substrates than on the other substrates.

The reactivity of the BisGMA/TEGDMA substrate can be related to the incomplete polymerization of the substrate. This could be explained by the finding that in the case of increasing concentration of the aromatic monomers (like BisGMA), the quantities of remaining methacrylate groups tend to increase [28]. Ruyter and Svendsen determined this by infrared reflectance measurements before polymerization and after polymerization [28]. The BisGMA/TEGDMA substrate used in the present study contained no filler particles. Ottaviani *et al.* [29] stated that the presence of inorganic fillers slowed the process of polymerization. Eliades *et al.* [30] noted that filler particles had an influence on the polymerization process. Li [31] found that the resin without fillers were least affected by surface treatments. The used particulate filler composite (Sinfony dentin) also has a high resin content, which gives it high potential for bonding to the surface by providing unreacted carbon-carbon double bonds. The behavior of the BisGMA/TEGDMA substrate and the progressive improvement of shear bond strength with the effect of IMR treating time are understandable from the findings of these previous studies. It should be emphasized also, that the delay from polymerization of the substrate to the bonding of new additional composite on the substrate surface could influence the remaining free radical activity of the substrate. It has been shown that for prolonged delay time the free radical activity is decreased [29]. By adding new composite resin on newly cured composite even though the oxygen-inhibition layer has been removed, the remaining free radical activity with the existence of unreacted $C{=}C$-bonds can result in high bond values based on free radical polymerization.

In FRCs glass fibers adhered to the polymer matrix by silane coupling agents which offer covalent and hydrogen bonding of polysiloxane network to glass fibers, and covalent bonding of functional groups of the coupling agent to the polymer matrix. In the case of FRC substrates a large proportion of the surface was glass fibers which were ground flat, which destroyed the polysiloxane network surface containing functional groups for free radical polymerization. This layer could have offered bonding of the resin to the glass surface. From this perspective, it might be beneficial to use silane coupling agents in bonding of the additional composite to the ground FRC substrate. The preliminary findings by the research group of Regensburg University also suggest this [32].

From the clinical perspective, IMR treatment time had no major effect on bond strength, except in the case of the BisGMA/TEGDMA substrate. However, it should be emphasized that the IMR used did not contain monomers of MMA or hydroxyethyl methacrylate, which could have behaved as solvent for linear polymer containing substrates. This limits the use of Sinfony activator resin to be used in further-impregnation of polymer-preimpregnated fibers only. The results of this study suggest that it is beneficial for bond strength to treat the BisGMA/TEGDMA substrate for at least 3 min with IMR if the clinical situation allows that. In clinical use, longer IMR treating periods are often too complicated, but in the case of laboratory repairs or during manufacturing a FRC appliance, longer IMR treatment times could be put in practice when BisGMA/TEGDMA based substrates are in use.

5. Conclusions

Within the limits of this study, the following conclusions were made:

1. Diacrylate IMR (Sinfony activator) did not form IPN bonding even with long application times.
2. BisGMA based substrate was adhered with most durable bond to the particulate filler composite.
3. It is beneficial to treat BisGMA based substrates with IMR at least 3 min to achieve maximum repair bond strength.

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