المرارف المراوف المرار

J. Adhesion Sci. Technol., Vol. 18, No. 15-16, pp. 1723-1737 (2004)
© VSP 2004.
Also available online - www.vsppub.com

The effect of hyper-branched polymers on the properties of dental composites and adhesives

H. DODIUK-KENIG 1,2,*, K. LIZENBOIM 2, I. EPPELBAUM 2, B. ZALSMAN 2 and S. KENIG 1

¹ Shenkar College for Engineering and Design 12 Anna Frank St., Ramat-Gan 52526, Israel

² BJM Laboratories Ltd., 12 Hassadna St., Industrial Park, Or-Yehuda 60200, Israel

Received in final form 27 September 2004

Abstract—With the emergence of commercial hyper-branched (HB) and dendritic polymers, having a three-dimensional (3D) morphology with high peripheral functionality, new opportunities have been created for formulating dental adhesives and composites with enhanced mechanical and physical properties. The objective of the present study was to investigate the properties obtained by incorporating HB and dendritic polymers into acrylate-based dental composite and adhesive systems. Four commercial HB polymers were evaluated: Polyamidoamine dendrimer, two dendripolyamides and HB polyesteramide. These were added to dental restorative glass filled prepolymers, based on BisGMA. HEMA and TEGDMA. The dendritic and HB polymers blended readily with the prepolymers. A significant effect of HB polyesteramide (HB1), addition (0.1-3.0 wt%) on the mechanical properties was shown. It was found that addition of 0.3 wt% (optimal value) of HB polyesteramide raised the compressive strength from 253 \pm 20 MPa to 386 \pm 20 MPa and lowered the linear shrinkage from 2.4 \pm 0.2% to 1.5 \pm 0.2% (for a model dental composite formulation). It was shown that the HB polyesteramide added to the dental adhesive compositions increased the shear bond strength and enhanced the bond durability to a variety of dental surfaces.

Keywords: Dental adhesives; dental composites; hyper-branched polymers; compressive strength; linear shrinkage.

1. INTRODUCTION

Amalgams have been used for dental restoration since the early 19th century and are still part of everyday dental practice [1].

The main challenge in dental restoration is to mimick and enhance the amalgam's dimensional stability and strength using polymer systems. Nevertheless, polymer

^{*}To whom correspondence should be addressed. Tel.: (972-3) 6110-000/257. Fax: (972-3) 619-0013. E-mail: hannad@mail.shenkar.ac.il

systems do not meet all the requirements such as high compressive strength, high modulus of elasticity and low values of shrinkage and micro-leakage.

1.1. Polymer dental composites

Dental composites are usually made with a hydrophobic resin and an inert filler. Resin cure is accomplished by free radical polymerization initiated by light and/or activators. These composites possess outstanding compressive (200 to 500 MPa) and flexural (130 to 170 MPa) strengths [2]. In addition, they are highly aesthetic and wear-resistant. However, a relatively high bulk shrinkage of 2.5 to 4.0% occurs during polymerization, which is a major drawback with regard to microfractures (Refs [3-8] and B. M. Culbertson, Q. Wan and S. R. Schricker, personal communication).

Modern composite systems contain fillers such as quartz, colloidal silica, silicaglasses containing strontium or barium. These fillers increase the strength and rigidity and reduce the polymerization shrinkage, the coefficient of thermal expansion and water sorption.

1.2. Polymer dental adhesives

The foundation of adhesive dentistry dates back to 1955 when Buonocore used commercial bonding techniques and acids for surface treatment before application of the resins [9]. Early attempts to adhesively bond dentin resulted in poor adhesion strengths [10]. This is not surprising given the fact that while enamel contains little protein, dentin comprises 17% of collagen by volume. The dentinal tubules are the only pores available for micro-mechanical retention. However, since these tubules contain liquid, durable adhesion cannot be developed.

Chronologically, dental adhesives may be categorized according to their generations — first to sixth [12-18].

1.3. Hyper-branched and dendrimer polymers

Flory first introduced the concept of hyper-branched (HB) polymers in 1952 [19]. The interest in HB polymers arose in the 1990s [20–22]. A wide variety of HB polymers have been reported in the literature, including polyesters, polyethers, polyphenylenes, polyurethanes, poly(ether ether ketone)s and polyamides. One feature of HB polymers is their low viscosity compared to linear analogs at the same molecular weight level.

1.4. Dental materials containing HB and dendrimer polymers

The combination of hyper-branched and dendrimer polymers with typical monomers commonly used in formulating dental composites seems to be a promising route for modification and improvement of dental restoratives properties.

Klee et al. [7] developed a low shrinking polymerizable dental material, which has bulk polymerization shrinkage of less than 1.5%.

Culbertson et al. (personal communication) have developed techniques to functionalize the hyper-branched polyesters (Boltron®, supplied by Perstrop, Sweden), obtaining polymerizable oligomers having C=C double bonds, i.e., methacrylate residues. These oligomers were used to modify a bisphenylglycidylmethacrylate (BisGMA)/tetraethylglycidylmethacrylate (TEGDMA) to formulate visible-light-curable (VLC) formulations having improved properties.

Sorensen et al. [23] developed a partially or fully cured thermosetting product. The composition included 70-99 wt% thermosetting resin and 1-30 wt% toughener agent. The toughener included a hyper-branched dendritic macromolecule formed of ester units, optionally in combination with ether units.

2. OBJECTIVES AND METHODOLOGY

The objective of the current study was to evaluate how the presence of hyperbranched and dendrimer polymers affected dental composite and adhesive properties. This investigation has been directed toward low shrinkage and high-strength dental composites and adhesives polymerized by chemical, light and dual (chemical + light) means. The methodology that has been used is to replace part of the 2,2-bis-[p-(2-hydroxy-3-methacryloyloxypropoxy)-phenyllpropane (Bis-GMA) used in conventional formulations with a hyper-branched or dendrimer polymer. The replaced amount was in the range of 0.1 wt% to about 3.0 wt%.

The hyper-branched polymers contained amide or hydroxyl end groups, while the dendrimer component contained carboxylate end groups.

In each case, the relationship between the maximum achievable compressive strength combined with the minimum obtained shrinkage was studied with respect to the type and amount of HB or dendrimer polymer used.

3. EXPERIMENTAL

3.1. Materials

- 3.1.1. Polymer dental composites.
- 3.1.1.1. Composite formulations. The materials used in dental composites are given in Tables 1 and 2.

The composite is highly-filled dental cement consisting of two parts: base and catalyst, polymerizing chemically by oxidization reaction when mixed in equal amounts.

The basic dental composite formulation without any dendritic component is given in Table 3. On the basis of this formulation, dental composites containing HB1, HB2, HB3 and HB4 were formulated.

Table 1.Resin and fillers used for dental composites

Component	Description				
Organic resin matrix	Acrylic mono- or multifunctional monomers and oligomers				
Inorganic filler	Silica glass containing strontium, barium; quartz; colloidal silica				
Accelerator for polymerization	Phosphorylated acrylate				
Photosensitizers for light curing	• • •				
Initiators for polymerization	Tertiary amine and benzoyl peroxide				
Dendritic component	Hyper-branched polyesteramide or				
·	hyper-branched polyamide oligomer or polyamidoamine				

Table 2. HB additives

Component	Brand name, manufacturer	Description Hyper-branched polyesteramide		
нв1	Hybrane™, DSM (The Netherlands)			
HB2	Epox™, Epox (Israel)	Hyper-branched polyamide with a hexavalent semi-flexible core		
IIB3	Epox [™] , Epox (Israel)	Hyper-branched polyamide with a tetravalent rigid core		
HB4 MW1	Boltom TM , Perstorp (Sweden)	HB polyester		
HB4 MW2	Boltom™, Perstorp (Sweden)	IIB polyester		

In order to allow comparison and study the effect of the dendritic moiety, commercial composites were also studied as detailed in Table 4.

3.1.1.2. Composite properties. Compressive strength test was carried out using a mechanical tester in accordance with ISO 9917. The crosshead speed was 0.5 mm/min and 10 specimens were prepared for each formulation.

For compressive strength tests cylindrical specimens, 4.0 ± 0.1 mm in diameter and 8.0 ± 0.1 mm in length, were made using split Teflon® moulds. Specimens were prepared using a layering technique in which the mold was filled with small amounts of material, which was then compacted. All specimens were kept at room temperature for 1 h and then immersed in water at $37 \pm 1^{\circ}\text{C}$ for 24 h prior to measurements. The values of water sorption, W_{sp} , and solubility, W_{sl} , in $\mu g/\text{mm}^3$, were calculated according to ISO 4049: 2000(E).

Table 3.
Basic dental composite formulation

No.	Base	Base		
	Material	wt%	Material	wt%
1	Bis-GMA	14.000	Bis-GMA	13,400
2	НЕМА	15.000	TEGDMA	13.080
3	DHEPT	0.400	Benzoyl peroxide	0,400
4	Filler	70.583	Filler	73.100
5	BHT	0.017	BHT	0.020
∑ (%)		100		100

Filler used for the two parts of the basic composition contained 97 wt% silanized glass and 3 wt% colloidal silica. Bis-GMA, bisphenylglycidylmethacrylate; TEGDMA, tetraethylglycidylmethacrylate; HEMA, 2-hydroxyethylmethacrylate; DHEPT, n,n-dihydroxyethyl-p-toluidine; BHT, 2,6-di-tert-butyl-4-methylphenol; 4-META, 4-methacryloxyethyltrimellitic acid.

Table 4. Commercial dental composites studied

Composite	Manufacturer	Description
Chemically polymerizable	le resin based dental composites	
Ti-Core	EDS (USA)	 Titanium-reinforced core Material releases fluorine
Encore	Centrix (USA)	 Self-cure composite resin Core paste with fluorine
CorePaste	DenMat (USA)	Core build-up materialSelf-cure
Dual polymerizable resir	based dental composites	
Build-it FR	Jeneric/Pentron (USA)	 Dual-cure fiber Reinforced core build-up
ParaCore	Coltene (USA)	 Dual-cure core build-up
LuxaCore	DMG (Germany)	 Dual-cure core build-up
Absolute Dentin	Parkell (USA)	 Dual-cure core build-up
Light polymerizable resi	n based dental composites	
TetricCeram	Ivoclar-Vivadent (Liechtenstein)	 Light-cured resin-based restorative material
Encore	Centrix (USA)	 Light-cured resin-based restorative material

For linear shrinkage measurement, glass tubes of 4.15 mm diameter were filled with composite material which self-polymerized by a free-radical mechanism. 5 specimens were prepared for each formulation. For testing the linear shrinkage, the length (height of the polymerized specimens) was measured using an optical microscope (magnification $\times 10$). The measurements were carried out during the

polymerization just after the beginning, and at 5, 10 and 60 min from the test initiation, as well as after immersion in water at $37^{\circ} \pm 1^{\circ}$ C for 24 h.

The exotherm temperature was measured for the chemically cured composition case. The highest temperature of the polymerization reaction was measured using a thermocouple.

3.1.2. Polymer dental adhesives.

3.1.2.1. Adhesive formulations. The neat dental adhesive formulation used without any dendritic component is given in Table 5. On the basis of this formulation, dental adhesive-HB1 and dental adhesive-HB2 formulations were produced. Table 6 describes the formulation of the polymer dental adhesive containing fillers. This formulation was based on commercial product (High-O-Bond, BJM, Israel).

Table 5.

Neat polymer dental adhesive formulation

No.	Material	wt%		
1	TEGDMA	21.00		
2	HEMA	12.00		
3	Urethanedimethacrylate oligomer	42.00		
4	Phosphorinated acrylate	5.00		
5	Photoinitiators	0.54		
7	Cross-linking agents	4.46		
8	Acrylic monomer	15.00		
$\sum (\%)$		100.00		

Table 6.
Polymer dental adhesive containing filler (High-Q-Bond)

No.	Base	Catalyst		
	Material	wt%	Material	wt%
I	Urethanedimethacrylate oligomer	36.40	Bis-GMA	24.20
2	HEMA	14.60	TEGDMA	17.00
3	Photoinitiators	1.00	4-META	1.72
4	Aluminoborosilicate	46.00	Benzoyl peroxide	80.0
5	Fumed silica	1.70	Aluminoborosilicate	54.70
6	TiO ₂	0.30	Fumed silica	20.00
			TiO ₂	0.30
∑ (%)		100		100

Samples were prepared to determine the effect of dendritic additives on the mechanical properties of the different formulations. A wide range of dendritic additive concentrations (0.1-3.0 wt%) was used.

3.1.2.2. Adhesive properties. The shear bond strength (SBS) of light-cured adhesive to dentin was determined using a mechanical tester and appropriate loading device for dental restorative materials. This test was conducted using bovine teeth first potted in poly(methyl methacrylate) and then ground and polished to expose the dentin. Dentin surface was acid treated (37% phosphoric acid) for 20 s and water rinsed. Following application of the adhesive (20 s) the surface was air dried and then light cured for 10 s. A second application of the adhesive was carried out followed by air-drying and light curing for 10 s. A gelatin capsule technique [24] was used in which a resin cylinder of 4.5 mm in diameter was used. A composite ('Lumifil anterieur', R&S, France) was used to fill the capsules approximately 2/3 full and then cured in a curing unit (Astralis 7, Vivadent, Leichtenstein) for one minute. Additional composite was added to slightly overfill the capsules. The specimens were additionally light cured for 20 s. Then, cylinders of composite resin were bonded to the tooth surface. After bonding and curing the sample, specimens were placed in water at 37°C for 24 h.

4. RESULTS AND DISCUSSION

4.1. Polymer dental composites

4.1.1. Effect of filler. The stiffness and strength of a composite is affected by the modulus of both filler and matrix, the filler loading, the aspect ratio (ratio of length to diameter), the filler-polymer interaction and the orientation of the particles within the matrix. Usually, as the stiffness increases, the composite brittles and, consequently, toughness decreases. However, depending on the type of polymer and filler, there are exceptions [25]. In most composite restorative materials, the final set of material contains around 70% filler [25, 26].

The neat dental composite without hyper-branched additives was tested to determine the effect of filler concentration in the composition.

Several compressive and linear shrinkage tests were conducted for filler concentrations of 57, 62.5, 68 and 73 wt%. Figures 1 and 2 indicate that the optimal amount of filler in the dental composite formulation was in the range 68–70 wt% as reported in the literature [26]. The relatively lightly filled formulations (57–63 wt% of filler) were characterized by considerably higher shrinkage than the more highly filled. However, at higher concentration of the filler (73 wt%) an increase of shrinkage was observed.

4.1.2. Effect of dendritic and hyper-branched polymers. The effect of hyper-branched polymers and dendrimers on the composite properties was investigated.

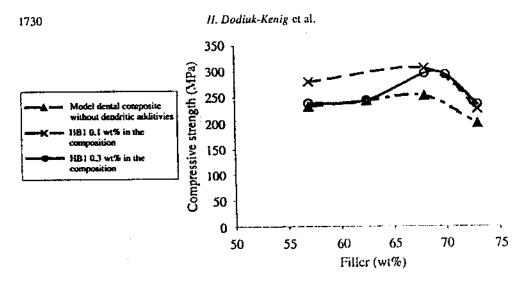


Figure 1. Compressive strength as a function of filler and HB contents in the model dental composite system.

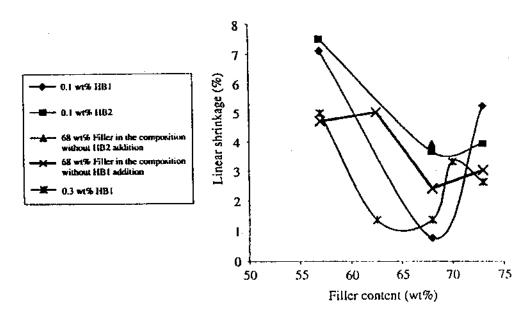


Figure 2. Linear shrinkage as a function of HB and filler contents in the model dental composite.

The results obtained (according to ISO 9917) for dental composite formulations containing HB polymers are presented in Figs 3-5.

A 0.3 wt% addition of polyesteramide (HB1 (optimal value)) resulted in an increase of the composite compressive strength (from 253 \pm 20 MPa to 386 \pm 20 MPa) and in a decrease of linear shrinkage (from 2.4 \pm 0.2% to 1.5 \pm 0.2%). However, at the same time the hexa-functional amidoamine HB polymer (HB2) decreased the compressive strength.

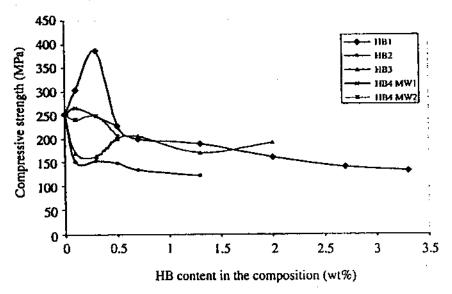


Figure 3. The effect of HB polymer on compressive strength of chemically-polymerized model dental composite.

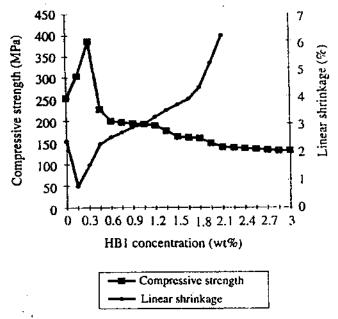


Figure 4. Compressive strength and Linear shrinkage as a function of HB1 concentration in chemically-polymerized model dental composite.

When a higher HB1 concentration was used, the linear shrinkage observed was higher than at the low HB1 concentration, but lower than the reference formulation. In addition, the tetra-functional amidoamine HB polymer (HB3), the

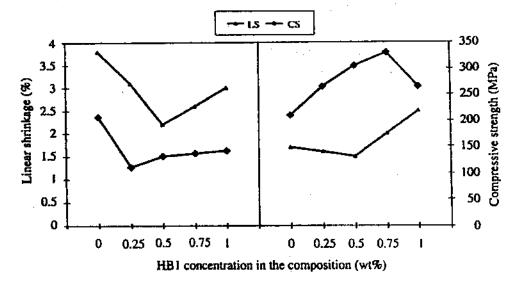


Figure 5. (Left) Mechanical properties of light-polymerized dental composite as a function of HB1 concentration in the composition mixture of fully silanized glass powder. (Right) Mechanical properties of light-polymerized dental composite as a function of HB1 concentration in the composition mixture of non-silanized and silanized glass powders.

low-molecular-weight HB polymer (HB4 MW1) and the high-molecular-weight HB polymer (HB4 MW2) were shown to be inefficient as reinforcing agents. This may be due to a fundamental difference in the chemical structures of the polymers and their compatibility with the resin system.

The hyper-branched polyesteramide (HB1) used in the current work is characterized by a cyclic structure having an amide nitrogen atom at the branching points and with 8 hydroxyl end groups having a molecular weight of 1500.

Polyamide HB2 is a highly branched oligomer with molecular weight of 12 100. It contains free reactive amidoamine groups in its structure. For multi-methacrylate polymerizable dental compositions only the hydroxyl groups of the HB1 are compatible, provided an optimal molecular weight in the range of 1200 is used.

Compared to the model composite, enhanced properties were obtained when adding hyper-branched polymer. Consequently, a novel composite (Q-Core Chemically Cured, BJM) for high strength was developed. The new composition contains hyper-branched polyesteramide (0.3 wt%) and a filler level of 71 wt%. The new composite consists of two parts base and catalyst and polymerizes chemically when mixed in equal amounts. The composite consists of the same components as the base one.

However, the filler levels are different for the base and the catalyst. The changes in filler content were dictated by aesthetic demands and desired additional properties: easy handling, high thermal conductivity and high fluorine-release.

Table 7.

Mechanical properties of various chemically polymerized composites

Property	ISO4049: 2000(E)	TiCore (EDS, USA)	CorePast (Den Mat, USA)	EnCore (Centrix, USA)	Q-Core chemically polymerized (BJM, Israel)
Compressive strength (MPa)	120.0	193.0	137.8	182.0	250.0
Linear shrinkage (%)	3.5	1.6	4.6	1.4	1.5
Water sorption (μg/mm³)	<40.0	5.5	2.2	3.4	23.8
Working time (min)	1.5	2.0	2.5	2.8	2.5
Sctting time (min)	5.0	4.5	5.0	4.7	5.0
Exotherm temp.	<41.0				39.0

Standard deviation is $\pm 10\%$.

A comparison between the newly developed composite and the commercial composites was carried out. The comparative physical and mechanical properties of the different commercial materials are summarized in Table 7.

As evident, the compressive strength for the novel composite was significantly higher than for the other materials tested at the same conditions. Only Q-Core Composite demonstrates compressive strength values (250 ± 20 MPa) similar to that of dentin (approximately 270 MPa) [28]. This composite tends to shrink less than the other commercial composites. However, it has a higher water sorption value than the other core build-up materials but less than the maximum value allowed by ISO 4049 (40 Mg/mm³). Furthermore, the composite complies with the requirements of ISO 4049 for setting time. The maximal heating temperature of the novel formulation meets the international standard requirements.

On the basis of the enhanced properties obtained for chemically cured Q-Core, the dual and light Q-Core Composites were developed.

- Light polymerized: 0.5 wt% of HB1 (optimal value) resulted in an increase of composite compressive strength (from 210 ± 20 MPa to 304 ± 20 MPa) and tensile strength (from 26 ± 3 MPa to 43 ± 3 MPa) and in a decrease of linear shrinkage (from 1.7 ± 0.2% to 1.5 ± 0.2%) (see Fig. 5a, 5b and Table 8).
- Dual polymerized: The physical and mechanical properties of the 0.3 wt% HB1containing dual polymerized fluorine-releasing composite (Q-Core) and of the conventional commercial ones are summarized in Table 9.

The Q-Core composition tends to shrink significantly less than the other commercial core build-up composites (1.2%). It also has the highest elastic modulus (8 GPa), hardness (90.2) and the most compatibility with different light sources.

Table 8.

Mechanical properties of various light polymerized composites

Property	Requirements according to ISO4049: 2000(E)	TetricCeram, (Ivoclar- Vivadent, Liechtenstein)	Encore, (Centrix, USA)	Q-Core light polymerized, (BJM, Israel)
Compressive strength (MPa)	120.0	105.0	170.0	304.2
Linear shrinkage (%)	3.5	2.7	2.0	1.5
Flexural strength (MPa)	50.0	85.9	90.0	105.0
Tensile strength (MPa)	40.0	46.5	35.8	42.7
E-modulus (MPa)	5000	6585	7405	8560
Solubility in water (µg/mm ³)	<7.5	0.1	2.9	1.0
Water sorption (µg/mm³)	<40.0	6.0	11.4	6.0

Standard deviation is ±10%.

Table 9.

Mechanical properties of various dual polymerized composites

Property	Requirements according to ISO4049: 2000(E)	Bulid-lt FR, (Jeneric/ Pentron, USA)	(Coltene,	LuxaCore, (DMG, Germany)	Dentin,	dual
Compressive strength (MPa)	120.0	221.0	230.0	260.0	235.7	251.0
Linear shrinkage (%)	3.5	2.0	2.7	2.7	4.0	1.2
Flexural strength (MPa)	50.0	60.0	90.0			68.3
Tensile strength (MPa)	40.0	41.1	50.2	24.0	41.3	40.0
E-modulus (MPa)	5000	6631	7786			8193
Solubility in water (µg/mm3)	<7.5	6.1	0.0	4.8		2.0
Water sorption (µg/mm ³)	<40.0	16.8	24.0	31.5		30.0
Hardness by Techlock Durometer GS-709N, type A		84.0	86.0	89.0	89.0	90.2
Setting time (min)	5.0	5.0	5.0	5.0	3.5	4.5
Exotherm temp. (°C)	<41.0	31.9	36.3		39.7	39.0

Standard deviation is $\pm 10\%$.

4.2. Polymer dental adhesives

4.2.1. Effect of dendritic and hyper-branched polymers on adhesive properties. Shear bond strength (SBS) was also evaluated. The shear bond strength results for

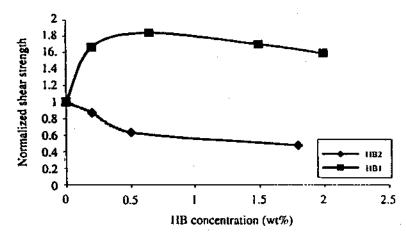


Figure 6. Normalized shear strength to bovine dentin etched with phosphoric acid (37%) as function of HB concentration in the model dental adhesive composition.

neat (filler free) polymer dental adhesive containing HB1 and HB2 formulations are given in Fig. 6.

The adhesive composition with HB1 addition in the range of 0.2-2.0 wt% demonstrates high bond strength to dentin. The optimal HB1 concentration is 0.65 wt%. HB2 addition reduced the SBS value of the basic adhesive.

The hyper-branched polyesteramide (HB1) was added also to polymer dental adhesive containing filler (commercial dual-cured adhesive system High-Q-Bond). Shear bond strength to cobalt-nickel alloy (RexilliumTM) substrate, commonly used in teeth repair, was employed. Compressive tests were carried out to investigate and optimize the hyper-branched polymer content.

Shear bond strength (SBS) to RexilliumTM was measured in same the way as to bovine dentin. RexilliumTM discs were first potted in poly(methyl methacrylate) and then ground and polished to expose the smooth surface.

Tests results are shown in Fig. 7, for chemically cured formulation. The optimum amount of HB1 is in the range 0.45-1.00 wt%, where the maximum increase in shear strength is obtained; at higher HB1 concentrations the strength decreased. Hyper-branched components cause higher cross-link density, which results in higher stiffness of the adhesive. With increased stiffness, the adhesive brittles and, consequently, loses toughness. This results in increased shear and decreased compressive strength. Above 1.00 wt% HB1, the plasticizing effect dominates resulting in both reduced shear [27] and compressive strengths.

Thus, the addition of hyper-branched polyesteramide is beneficial to obtain higher strength and more durable bonds to different surfaces and can be used in chemically or visible-light-curing adhesive systems.

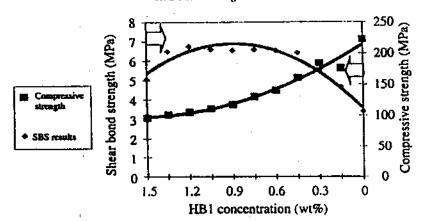


Figure 7. Shear bond strength (SBS) to Rexillium[™] and compressive strength as function of HB1 concentration in the High-Q-Bond adhesive resin cement (BJM, Israel) composition.

5. CONCLUSIONS

- The mechanical properties of dental composites improved significantly due to the
 incorporation of hyper-branched (HB) polyesteramide. The other HB polymers
 did not show the same behavior. These differences in behaviors may be due to
 the fundamental difference in the chemical structures of the HB polymers.
- Addition of hyper-branched polymer causes higher cross-link density as a result
 of the large number of reactive end groups on the periphery that can react with the
 constituents of the polymer network. The enhanced cross-linking leads to higher
 compressive strength and lower polymerization shrinkage. At concentrations
 higher than 0.5 wt%, the HB polymer acts as a plasticizer, reducing compressive
 strength and increasing shrinkage.
- Hyper-branched polyesteramide increased the shear strength of dental adhesive compositions and enhanced their bond durability to a variety of dental surfaces.
- The current study resulted in the development of novel dental composites and adhesives, having significantly enhanced properties with combined effect of both strengthening and toughening of the polymers [28]. This may be attributed to the new architectures and associated formation of 3D morphologies as a result of the hyper-branched polymers having appropriate functional end-groups, leading to a modified molecular network.

REFERENCES

- 1. R. van Noort, Introduction to Dental Materials. Mosby, St. Louis, MO (1994).
- J. E. Klee, F. Neidhart, H. J. Flammersheim and R. Mulhaupt, <u>Macromol. Chem. Phys.</u> 200, 517 (1999).
- 3. C. M. Sturdevant, The Art and Science of Operative Dentistry, 3rd edn. Mosby, St. Louis, MO (1995).

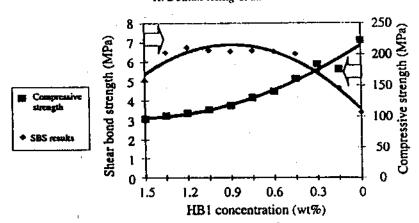


Figure 7. Shear bond strength (SBS) to RexilliumTM and compressive strength as function of HB1 concentration in the High-Q-Bond adhesive resin cement (BJM, Israel) composition.

5. CONCLUSIONS

- The mechanical properties of dental composites improved significantly due to the
 incorporation of hyper-branched (HB) polyesteramide. The other HB polymers
 did not show the same behavior. These differences in behaviors may be due to
 the fundamental difference in the chemical structures of the HB polymers.
- Addition of hyper-branched polymer causes higher cross-link density as a result
 of the large number of reactive end groups on the periphery that can react with the
 constituents of the polymer network. The enhanced cross-linking leads to higher
 compressive strength and lower polymerization shrinkage. At concentrations
 higher than 0.5 wt%, the HB polymer acts as a plasticizer, reducing compressive
 strength and increasing shrinkage.
- Hyper-branched polyesteramide increased the shear strength of dental adhesive compositions and enhanced their bond durability to a variety of dental surfaces.
- The current study resulted in the development of novel dental composites and adhesives, having significantly enhanced properties with combined effect of both strengthening and toughening of the polymers [28]. This may be attributed to the new architectures and associated formation of 3D morphologies as a result of the hyper-branched polymers having appropriate functional end-groups, leading to a modified molecular network.

REFERENCES

- 1. R. van Noort, Introduction to Dental Materials, Mosby, St. Louis, MO (1994).
- J. E. Klee, F. Neidhart, H. J. Flammersheim and R. Mulhaupt, Macromol. Chem. Phys. 200, 517 (1999).
- 3. C. M. Sturdevant, The Art and Science of Operative Dentistry, 3rd edn. Mosby, St. Louis, MO (1995).