



# Evaluation of Hyperbranched Polymers Effect on Dental Composite Properties

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## Introduction

The introduction of novel macromolecular architectures based on new developed dendritic nanotechnology systems enable us to tailor properties for dental requirements. Among the new architectures are those related to hyper-branched and dendritic polymers.

**WHAT ARE DENDRIMERS?**

- Resemble dendritic structures
- Spherical structures with peripheral functional groups.
- The dendrimers synthesis is a function of the dendrimers' generations based on the strategy of the repetitive synthesis.
- Relatively expensive materials.

**WHAT ARE HYPER-BRANCHED?**

- Highly branched but lower branching degree than dendrimers.
- Non-linear shaped with high number of reactive end groups.
- Preparation is much simpler than that of dendrimers.
- Low cost price materials.

The incorporation of hyper-branched polymers and dendrimers, which are low viscosity materials compare to linear polymers at the same molecular weight level, to the commonly used monomers in formulating dental composites, have recently attracted attention with the aim to form novel morphologies and consequently enhanced dental related characteristics.

**The unique architecture and chemical structure of the macromolecule shell, leads to potential novel polymer network and tailored mechanical properties.**

## Objectives

To study the new associated dental composites properties obtained by incorporating highly branched polymers and dendrimers into commonly used dental systems:

- Primer
- Adhesive
- Composite
- Coating

The effort was directed toward a low shrinkage, high strength composite based dental materials.

## Methodology, Materials and Methods

The base composites formulations contained BisGMA, HEMA and TEGDMA, and filled with glass powder. The above compositions were polymerized chemically, or light or dual by free-radical mechanism.

**Five commercial dendritic polymers were selected:**

- ⇒ hyper-branched polyesteramide Hybrane™ (DP1) by DSM,
- ⇒ dendriopolyamides Epox™ (DP2, DP3) by Epox,
- ⇒ hyper-branched polyesters Boltorn™ (DP4MW1 & DP4MW2) by Perstorp.

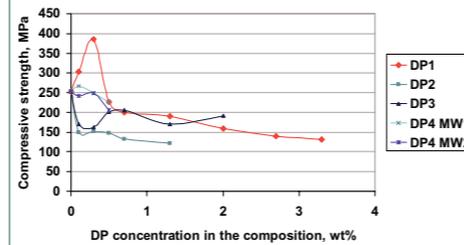
Their molecular weight ranged from 1,500 to 12,100, the functional groups were hydroxyls, amines or carboxylates having cyclic or aliphatic highly branched structure. The dendrimers and hyperbranched polymers were found to blend readily with the base monomers in a concentrations range of 0.1 to 10.0 wt%.

A variety of tests were used to evaluate the composites properties: compressive strength (ISO 9917), solubility and water sorption (ISO 4049), flexural strength (ISO 4049), diametral tensile strength (ISO 9917), hardness (by Barcol or Durometer), depth of cure (ISO 4049) and linear polymerization shrinkage (self developed method). The experimental results were analyzed statistically by ANOVA.

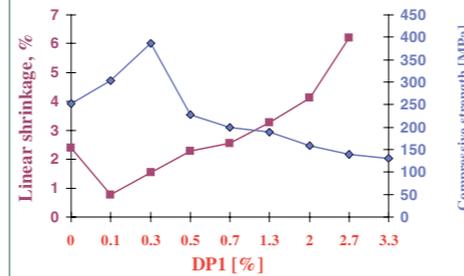
Commercially available dental composites were used as reference and were characterized under the same conditions.

## Results

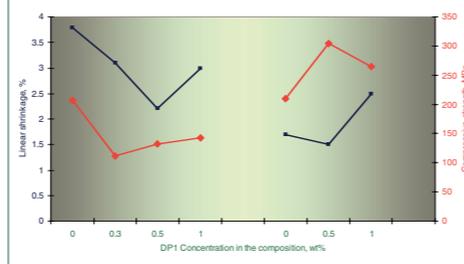
**Figure 1.** The effect of the dendritic polymer incorporation on the compressive strength of chemically polymerized dental composite



**Figure 2.** Compressive Strength [MPa] and Linear Shrinkage [%] as a function of DP1 concentration in chemically polymerized dental composite



**Figure 3.** Mechanical properties of the light polymerized dental composite as a function of DP1 concentration in the composition, filled by a mixture of non-silicized and silicized glass powders



**Figure 4.** Mechanical properties of the light polymerized dental composite as a function of DP1 concentration in the composition, filled by a mixture of fully silicized glass powders

**Table 1. Mechanical Properties\* of BJM Chemically polymerized Resin Based Composite Compared with Commercial Materials**  
 \* Standard Deviation is ±10%.

Properties	ISO4049: 2000(E)	TicCore EDS Inc.	CorePast DenMat	EnCore Centric Inc.	Q-Core chemically polymerized BJM Lab Ltd.
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/mm <sup>3</sup> ]	<40.0	5.5	2.2	3.4	23.8
Working Time [min]	1.5	2.0	2.5	2.8	2.5
Setting Time [min]	5.0	4.5	5.0	4.7	5.0
Exothermal Temp. [°C]	<41.0				39.0

**Table 2. Mechanical properties\* of BJM dual polymerized core build-up material compared with commercial composites**  
 \* Standard Deviation is ±10%.

Properties	Requirements According to ISO4049: 2000(E)	Bondic 95, 3M/3M	PerfCore, 3M	LeakCore, 3M	Absolute, Dentsply	Q-Core dual polymerized BJM Lab Ltd.
Compressive Strength [MPa]	120.0	221.0	230.0	200.0	235.7	251.0
Linear Shrinkage [%]	3.5	2.0	2.7	2.7	4.8	1.2
Flexural strength [MPa]	50.0	90.0	90.0			95.3
Diametral Tensile Strength [MPa]	40.0	41.1	50.2	24.0	41.3	46.0
E-Modulus [MPa]	5,000.0	6,875.0	7,786.0			8,193.0
Solubility [µg/mm <sup>3</sup> ]	<7.5	6.1	6.0	4.8		2.0
Water Sorption [µg/mm <sup>3</sup> ]	<40.0	16.8	24.0	31.5		36.0
Hardness by Tabrock Durometer (D5-703N), (µN)		84.0	90.0	89.0	88.0	96.2
Depth of cure [mm] (Insulation by Demetron (Mer) - dental LED lamp - for 10 sec.)	>2.0					2.2
Depth of cure [mm] (Insulation by Amlab 7 (Ultradent) - dental LED lamp - for 10 sec.)	>2.0	0.62	0.62	0.90	0.24	0.97
Setting Time [min]	5.0	5.0	5.0	5.0	3.5	4.0
Exothermal Temp [°C]	<41.0	31.0	30.3		30.7	35.0

**Table 3. Mechanical properties\* of BJM Light polymerized composite compared with commercial composites**  
 \* Standard Deviation is ±10%.

Properties	Requirements According to ISO4049: 2000(E)	TetricCeram, 3M	EnCore, Centric	Q-Core light polymerized, BJM Lab Ltd.
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
Diametral Tensile Strength [MPa]	40.0	46.5	35.8	42.7
E-Modulus [MPa]	5,000.0	6,585.0	7,405.0	8,560.0
Solubility [µg/mm <sup>3</sup> ]	<7.5	0.1	2.9	1.0
Water Sorption [µg/mm <sup>3</sup> ]	<40.0	6.0	11.4	6.0

The effect of dendritic polymer incorporation on:

**Chemically polymerized:**  
 0.3 wt% of DP1 (optimal value) resulted in the increase of the composite compressive strength (from 253±20 MPa to 386±20 MPa) and in the decrease of the linear shrinkage (from 2.4±0.2 % to 1.5±0.2 %) (see Figures 1,2).

**On the basis of those enhanced properties a new core composite (Q-Core, BJM) for high strength core build-up was developed** (see Table 1).

**Light polymerized:**  
 0.5 wt% of DP1 (optimal value) resulted in the increase of the composite compressive strength (from 210±20 MPa to 304±20 MPa) and the diametral tensile strength (from 26±3 MPa to 43±3 MPa) and in the decrease of the linear shrinkage (from 1.7±0.2 % to 1.5±0.2 %) (see Figure 3 and Table 3).

**Dual polymerized:**  
 The physical and mechanical properties of the 0.3wt% DP1- containing dual polymerized fluoride releasing composite (Q-Core) and of the conventional commercial ones are summarized in Table 2.

As can be seen Q-Core tends to shrink significantly less than the other commercial core build-up composites (1.2%). It also shows the highest values of elastic modulus (8GPa), hardness (90.2) and compatibility with the different light sources.

## Discussion

The properties of dental composites have improved significantly due to the incorporation of hyper-branched polymer (Hybrane™). However, the other hyper-branched polymers didn't exhibit the same behavior ( Epox and Boltorn) This phenomena may be due to the fundamental difference in the chemical structures of these dendritic polymers (Figure 1).

- The hyper-branched component causes higher cross-linking density as a result of branching and the number of reactive end groups. The enhanced cross-linking results in higher compressive strength and decreased polymerization shrinkage and toughness. (This is probably the explanation at low Hybrane™ values, Figures 2,3.)
- At higher than 0.5wt% concentration the dendritic polymer acts as plasticizer that may reduce the compressive strength and increase linear shrinkage value. (Figures 1-3).
- Incorporation of a higher concentration than 0.1wt% of Epox (DP2 & DP3) and Boltorn (DP4 MW1 & DP4 MW2) dendritic polymers causes a plasticizing of the molecular network (Figure 1).
- Use of hyper-branched polymer in dental composite formulations provides additional beneficial rheological (handling) properties because of its low intrinsic viscosity, high solubility and miscibility.

## Conclusions

- Hyper-branched polyesteramide (DP1) incorporation exhibits a significant improvement of the dental composites properties at the range of 0.1-0.5 wt% Hybrane™ (a substantial reduction in shrinkage and a parallel increase in mechanical properties).
- It is shown that incorporation of other highly branched polyesters and dendriopolyamides into the dental composition didn't exhibit the similar improvement of mechanical properties.

*The present investigation resulted in the development of new dental composites, having significant enhanced properties with synergistic effect that exhibits both strengthening and toughening of the polymers. This may be attributed to the new architectures and associated morphologies that may be formed as a result of the hyper-branched polymers having appropriate functional end groups leading to a modified molecular network.*