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The mechanical stability of nano-hybrid composites with new methacrylate monomers for matrix compositions

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ABSTRACT

Objectives. Dimer acid based metacrylates and TCD-urethane are promoted as new monomers of nano-hybrid resin based composites as alternatives for the conventional BisGMA. Investigations of this study focused on the mechanical and the storage behavior of nano-hybrid resin based composites (RBCs) composed of these new types of monomers in comparison to RBCs using BisGMA.

Methods. Flexural strength and modulus were determined in a three-point-bending test. Additionally, the modulus of elasticity was measured on microscopic scale (E_{micro}) using an automatic microhardness indenter. Tests were performed on samples after 24 h storage in distilled water, as well as after thermocycling and storing the materials for four weeks in either distilled water, artificial saliva or ethanol.

Results. The six measured materials showed a pronounced decrease of flexural strength, flexural modulus and E_{micro} after four weeks storage in alcohol. Results after four weeks storage in water and saliva could not be proven to be significantly different. The most sensitive factor of influence on all test parameters was the material.

Significance. Nano-hybrid composites with new or conventional monomers performed similar in regard to the mechanical properties and the behavior of the materials after aging.

1. Introduction

The current trend toward minimizing filler size in order to achieve great optical qualities, and toward maximizing filler loading is an attempt to satisfy all of the requirements for dental composites [1]. Advantages named within the context of high filler loading of RBCs are improved mechanical properties [1–3], high wear resistance [4], and reduced polymerization shrinkage [1]. Nano-hybrid RBCs contain a range of different filler sizes, also large filler particles besides the eponymous nano scale sized fillers. The varying particle sizes provide for a homogenous filler distribution within the matrix, since the small nano fillers are able to occupy the spaces between the larger particles perfectly and therefore help to generate RBCs with filler loadings that are comparable with the conventional hybrid composites. Nano-hybrid RBCs are claimed to combine both the positive characteristics of macro-filled composites (such as excellent physical and mechanical properties) and of micro-filled ones (e.g. excellent finishing and polishing qualities) and thus can be recommended as universal filling materials for anterior and posterior restorations [5]. The matrix of most of these new types of composites still consists of the conventional BisGMA monomer developed by Bowen, yet new types of monomers have recently been introduced in the matrices of nano-hybrid composites, like the dimer acid based dimethacrylate monomer (N'Durance, Septodont), and a special urethane monomer, namely TCD-urethane (Venus

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Table 1 – Materials, manufacturers, chemical composition of the matrix and the filler and filler content by weight and volume % (content (w/v)).

Material	Manufacturer	Color	Lot-no.	Matrix	Filler	Content (w/v)
Grandio	Voco	A 3	0921103	BisGMA, UDMA, di-methacrylate, TEGDMA	Fluorosilicate glass, SiO_2	87/71.4
N'Durance	Septodont	A 3	G-9020-11	BisGMA, UDMA, dicarbamate dimethacrylate dimer acid	Ytterbium-fluorid, bariumglass, quarz	80/65
Venus Diamond	Heraeus	A 3	010029	TCD-DI-HEA, UDMA	Barium-aluminum-fluoride-glass	81/64
Miris 2	Coltène/Whaledent	S 2	0191818	Methacrylates	Bariumglass, SiO_2	80/65
Premise	Kerr	A 3	3120178	TEGDMA, BisGMA	Bariumglass, SiO_2, pre-polymerized fillers	84/71.2
Simile	Jeneric Pentron	A 3	190633	PCBisGMA, BisGMA, UDMA, HDDMA	Barium silicate-glass, circonium-silicate, SiO_2	75/66

Data are provided by the manufacturers.
BisGMA: bisphenol A diglycidyl methacrylate; UDMA: urethane dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; TCD-DI-HEA: 2-propenoic acid; (octahydro-4,7-methano-1H-indene-5-diyl) bis(methyleneiminocarbonyloxy-2,1-ethanediyl) ester; PCBisGMA: pentron clinical-bisphenol A diglycidyl methacrylate; HDDMA: hexanedioldimethacrylate.

Diamond, Heraeus Kulzer). The core structure of the dimer acid based monomer is composed of both linear and cyclic aliphatic structures [6]. "Dimer acid" means any of the class of cycloaliphatic carboxylic acids that are high-molecular-weight dibasic acids which are liquid (viscous), and which can be polymerized directly with alcohols and polyols to form polyesters [7]. The manufacturer promises both low volumetric shrinkage, and a high conversion rate. Two characteristics that do not seem compatible, but desirable in order to reduce stress on the tooth and in case of the conversion rate limit the elution of any residual monomer and thus enhance the biocompatibility of the material. This controversy is explained by the bulky nature of the core structure of the dimer acid based dimethacrylates. Because of their high molecular weight and a low initial double bond concentration, dimer acid monomers still have significantly lower polymerization shrinkage, despite of the high conversion rate achieved [6].

Only little information is available about the TCD-urethane monomer. According to information provided by the manufacturer, a low shrinkage crosslinker monomer with a special aliphatic structure has been synthesized. The new methacrylic acid derivatives, containing urethane groups of tricyclo-decanes are prepared by reaction of hydroxyalkyl (meth)acrylic acid esters with diisocyanates and subsequent reaction with polyols [8]. Similar to bisphenol-A, the structure of the TCD-urethane backbone was proven to be rigid [9]. In combination with the high reactivity of the urethane groups of the molecule, the new monomer is seen to be an alternative to BisGMA [9].

The aim of this study was to compare two nano-hybrid RBCs composed of new matrix monomers to conventional nano-hybrid RBCs available on the market, with regard to macro-mechanical properties, such as flexural strength and flexural modulus, and micromechanical measurements of the modulus of elasticity (E_{micro}). Furthermore the focus was laid on the behavior of nano-hybrid RBCs after aging and storage in three different solutions: distilled water, artificial saliva and a 1:1 alcohol–water mixture for 28 days, compared to 24 h water storage. Following null hypotheses were tested: nano-hybrid RBCs composed of new monomers, such as TCD-urethane or dimer acid based methacrylates, show no differences in the mechanical properties when compared to nano-hybrid RBCs using conventional BisGMA monomers. The behavior of all six measured materials is similar in the three storing conditions.

2. Materials and methods

The six measured materials were nano-hybrid RBCs. Material composition, lot numbers, colors and manufacturers are shown in Table 1.

Flexural strength and flexural modulus were determined in a three-point-bending test, using a universal testing machine (Zwick/Roell Z 2.5, AST. GmbH, Ulm, Germany). The bar-shaped specimen, measuring 2 mm × 2 mm × 16 mm, were produced by applying the composites to a stainless steel mold, and were then shaped between two parallel glass plates, covered with transparent matrix strips prior to light curing. Irradiation occurred on top and bottom of the specimens, with three light exposures of 20 s per side, overlapping one irradiated section no more than 1 mm of the diameter of the light guide (Elipar™ Freelight 2, 3M ESPE), in order to prevent multiple polymerization. After removal from the mold the specimens were grinded with silicone carbide paper (grit size P 1200/4000 (Leco)) in order to get rid of disturbing edges or bulges. 80 such specimens of each material were produced and then stored in distilled water for 24 h at 37 °C, 20 of them being loaded to fracture right after the 24 h water storage. The remaining 60 samples were thermocycled for 5000 cycles at 5–55 °C, before being randomly divided into groups of 20 specimens, stored in either distilled water, commercial artificial saliva (see Table 2 for composition) or a 50:50 mixture of