Properties evaluation of silorane, low-shrinkage, non-flowable and flowable resin-based composites in dentistry

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(Purpose) This study tested the null hypothesis that different classes of direct restorative dental materials: silorane-based resin, low-shrinkage and conventional (non-flowable and flowable) resin-based composite (RBC) do not differ from each other with regard to polymerization shrinkage, depth of cure or microhardness. (Methods) 140 RBC samples were fabricated and tested by one calibrated operator. Polymerization shrinkage was measured using a gas pycnometer both before and immediately after curing with 36 J/cm^2 light energy density. Depth of cure was determined, using a penetrometer and the Knoop microhardness was tested from the top surface to a depth of 5 mm. (Results) Considering polymerization shrinkage, the authors found significant differences ($p<0,05$) between different materials: non-flowable RBCs showed lower values compared to flowable RBCs, with the silorane-based resin presenting the smallest shrinkage. The low shrinkage flowable composite performed similarly to non-flowable with significant statistical differences compared to the two other flowable RBCs. Regarding to depth of cure, low-shrinkage flowable RBC, were most effective compared to other groups. Microhardness was generally higher for the non-flowable vs. flowable RBCs ($p<0.05$). However, the values for low-shrinkage flowable did not differ significantly from those of non-flowable, but were significantly higher than those of the other flowable RBCs. (Clinical Significance) RBCs have undergone many modifications as they have evolved and represent the most relevant restorative materials in today's dental practice. This study of low-shrinkage RBCs, conventional RBCs (non-flowable and flowable) and silorane-based composite – by in vitro evaluation of volumetric shrinkage, depth of cure and microhardness – reveals that although filler content is an important determinant of polymerization shrinkage, it is not the only variable that affects properties of materials that were tested in this study.

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26   **ABSTRACT**

27   (Purpose) This study tested the null hypothesis that different classes of direct restorative dental

28   materials: silorane-based resin, low-shrinkage and conventional (non-flowable and flowable) resin-

29   based composite (RBC) do not differ from each other with regard to polymerization shrinkage, depth

30   of cure or microhardness.

31   (Methods) 140 RBC samples were fabricated and tested by one calibrated operator. Polymerization

32   shrinkage was measured using a gas pycnometer both before and immediately after curing with 36

33   J/cm^2 light energy density. Depth of cure was determined, using a penetrometer and the Knoop

34   microhardness was tested from the top surface to a depth of 5 mm.

35   (Results) Considering polymerization shrinkage, the authors found significant differences (p<0,05)

36   between different materials: non-flowable RBCs showed lower values compared to flowable RBCs,

37   with the silorane-based resin presenting the smallest shrinkage. The low shrinkage flowable composite

38   performed similarly to non-flowable with significant statistical differences compared to the two other

39   flowable RBCs. Regarding to depth of cure, low-shrinkage flowable RBC, were most effective

40   compared to other groups. Microhardness was generally higher for the non-flowable vs. flowable

41   RBCs (p<0.05). However, the values for low-shrinkage flowable did not differ significantly from those

42   of non-flowable, but were significantly higher than those of the other flowable RBCs.

43   (Clinical Significance) RBCs have undergone many modifications as they have evolved and represent

44   the most relevant restorative materials in today's dental practice. This study of low-shrinkage RBCs,

45   conventional RBCs (non-flowable and flowable) and silorane-based composite – by *in vitro* evaluation

46   of volumetric shrinkage, depth of cure and microhardness – reveals that although filler content is an

47   important determinant of polymerization shrinkage, it is not the only variable that affects properties of

48   materials that were tested in this study.

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INTRODUCTION:

When dental resin-based composite (RBC) is light cured, stresses develop as a result of the polymerization contraction that accompanies setting, and they may be transferred to the bonded margins of the restoration[1-5]. The magnitude of these potentially damaging stresses is a function of certain characteristics of the material, such as its composition (particularly the filler concentration), the reaction kinetics and the degree of conversion of the polymeric matrix[1-4].

The filler content of each RBC is directly related to the mechanical properties and wear resistance of the polymerized product. High volume (%) of different fillers are fundamental to minimizing shrinkage of the composite during polymerization[6]. As the filler content influences both the elastic modulus and volumetric shrinkage, the amount of filler present in an RBC is a major determinant of polymerization contraction stress[7], which ultimately affects the integrity of the restoration margin[1-3].

Flowable RBCs differ from their conventional ("non-flowable") counterparts in that they contain substantially less (as much as 25% by weight) filler than conventional RBC[8], and several studies have shown significant differences in the elastic modulus and volumetric shrinkage between materials of these two classes[2,9]. Although the high volumetric shrinkage that characterizes flowable composite materials may lead to high stress values, it is possible that their low elastic modulus could compensate to some degree for the stress buildup, by helping to maintain the marginal seal and integrity of the restoration[2]. Although flowable RBCs generally have a lower elastic modulus than their non-flowable counterparts, in some cases the elastic modulus may not be low enough to provide significant stress relief, as has been observed in studies evaluating unfilled resins[1].

Efforts to overcome clinical deficiencies of RBCs have led to the development of new matrix materials[10]. Siloranes have been suggested as alternatives to methacrylates as components of the RBC polymer matrix, due to their hydrophobicity and low polymerization shrinkage[11-12]. Siloranes are

73   hybrid systems that contain both silorane and oxirane-based monomers. The individual components of

74   the base resin silorane combined provide two main advantages: low polymerization shrinkage, due to

75   ring opening of the oxirane monomer; and increased hydrophobicity, due to the nature of siloxane

76   species. This system compensates for contraction-induced stress by opening of the oxirane ring during

77   polymerization. The advantage of the hydrophobicity of this restorative material is that it leads to lower

78   absorption of pigments present in the diet, and may reduce the potential for the adhesion of oral

79   biofilms[12]. Additionally, silorane monomers produce RBC systems with better biocompatibility and

80   margin integrity, as well as lower water absorption and solubility relative to methacrylate-based

81   RBCs[13].

82   The aim of this study was to measure and compare polymerization shrinkage, depth of cure, and

83   Knoop microhardness (KHN) among low-shrinkage to conventional (non-flowable and flowable)

84   RBCs. The tested hypotheses are that: Silorane and low- shrinkage RBCs will present lower

85   polymerization shrinkage; overall shrinkage of the conventional flowable and non-flowable RBCs is

86   related indirectly to their filler content volumes; and low-shrinkage RBCs will have the greatest depth

87   of cure. Therefore this *in vitro* study tested the null hypothesis that different restorative materials:

88   low-shrinkage, conventional (non-flowable and flowable) RBCs and silorane not differ from each other

89   with regard to polymerization shrinkage, depth of cure and microhardness.

90

91   **METHODS AND MATERIALS**

92   **Materials selection and specimen preparation**

93   In this study, seven restorative dental materials (**Table 1**) of A2 / U shade were selected to

94   minimize the effects of colorants on the light polymerization. All samples were fabricated and tested

95   by one calibrated operator. Materials were evaluated for percentage of filler volume and matrix

96   monomer variation within the major categories of restorative RBC: conventional non-flowable (C),

97   flowable (F) or low-contraction (L). Regarding to the material type based on the filler size, 2 different

98   groups are present in this study: Nanofilled and Mycro-hybrid RBCs.

99

100   **Polymerization shrinkage**

101   Ten samples per group (n=70) were fabricated by placing the material in a 4 mm diameter by 2

102   mm height stainless steel molds. After the molds were filled, they were placed into a calibrated gas

103   pycnometer AccuPyc™ 1340, Micromeritics®, and the volume was measured before and after light

104   curing. Accuracy was ensured by measuring the volume of each specimen five times.

105   Photopolymerization was performed by using a glass slide (2mm thickness) on top of the mold to

106   support the polywave LED tip (Ultra-Lume LED5 at 600 mW/cm^2, Ultradent, South Jordan, UT, USA)

107   delivering 36 J/cm^2 (600 mW/cm^2 as measured with a LED radiometer 910726, Kerr, Orange, CA,

108   USA) of light energy to each specimen to ensure that all brands and ranges of materials were

109   completely cured.

110

111   The polymerization shrinkage was calculated using the equation:

112   $$PS = \frac{V_i - V_f}{V_i} \times 100$$

113   V_i

114   where PS is the polymerization shrinkage (in %), V_i is the volume of unpolymerized RBC and V_f is the

115   volume of polymerized RBC.

116

117   **Depth of cure**

118   There is disagreement over the best depth of cure evaluation for RBCs. Among the available tests,

119   those assessing the degree of conversion, microhardness and scraping are the most reliable[14].

120　Independent of the test used, the depth of cure needs to take into account the depth at which the

121　transition between the glassy and rubbery state of the resin matrix occurs[15].

122　　The depth of cure was determined using a circular stainless steel split mold (6mm diameter by

123　5mm height). Ten samples per group (n=70) were prepared by using the same light curing unit and the

124　amount of energy described previously. A Microtester (Instron Corporation, Model No. 4206) was

125　used as a penetrometer, according to the methodology of Harrington and Wilson (1993)[16]. Immediately

126　after light curing, the molds were inverted such that the unexposed surface (bottom) faced the

127　penetration needle. Pulses of a 12.5N force (1250 grams) were applied using a 0.5mm diameter needle,

128　at a rate of 1 mm/min, to the middle of the bottom, and the depth of penetration was measured digitally

129　at this point. Depth of cure was calculated using the formula: Depth of cure = Depth of mold - Depth of

130　penetration.

131

132　**Knoop microhardness (KHN)**

133　　After depth of cure was measured, the same specimens (n=70) were subjected to testing of KHN

134　using a Digital Microhardness Tester (Matsuzawa Co., Ltd. Model no. MMT-X7 Toshima, Kawabe,

135　Japan). The top, light-exposed surface of each specimen was placed directly below the Knoop diamond

136　indenter, and a 500g load was applied using the indenter, with a dwell time of 15 seconds. The

137　indentation on the top surface was measured at 100X magnification. The KHN corresponding to each

138　indentation was computed by measuring the dimensions of the indentation and using the formula KHN

139　= 14. 2 X (F/d^2), where F = test load in Newtons; d = longer diagonal of an indentation (in mm). After

140　determining the KHN at the top surface, the split stainless steel mold was opened and KHN values of

141　the side surfaces of the RBC specimens were measured, at 1-mm intervals and working from the top

142　surface down to the level determined as the depth of cure of the RBC sample, using the testing

143　parameters described above. The bottom value for KHN was then recorded.

144

145 **Statistical analysis**

146   Statistical analysis was performed using a one-way analysis of variance (ANOVA) and a post-hoc

147 test of Student-Newman-Keuls (SNK) to segregate the materials into groups of similar behavior.0.05

148 was considered the cutoff for significance.

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151 **Results**

152   The results obtained in the present study are displayed in **Table 2.** Included are mean values

153 ($p<0.05$) and for the degree of polymerization shrinkage, depth of cure and KHN for each RBC. One-

154 way ANOVA indicated that in each test at least one RBC produced statistically significant differences

155 ($p<0.05$) from the others.

156   Regarding to:

157   1) Polymerization shrinkage, the statistical analysis for the seven composite resins revealed

158 statistically significant differences. FP90 (which is based on the resin silorane) showed the lowest

159 value for shrinkage, followed by the non-flowable RBCs (Tetric N Ceram, Filtek Z350XT and Esthet-

160 X HD). SDR represents an intermediate group, with lower values of shrinkage than the other flowable

161 RBCs (FZ350F and TNF).

162   2) Depth of cure, the RBCs fell into three distinct groups. SDR exhibited the highest depth of cure.

163 A group of flowable RBCs formed the second group. The non-flowable RBCs represent the third

164 group.

165   3) Knoop microhardness, values for the seven composite resins varied widely. As expected, the

166 highest values for hardness at the top surface were exhibited by the non-flowable RBCs. Moreover,

167 when the KHN values at the bottom were evaluated, SDR had the highest value.

168

169   **Discussion**

170   The results obtained in this analysis led to rejection of the stated null hypothesis, with the tested

171   RBCs showing distinct qualities with regard to polymerization shrinkage, depth of cure and

172   microhardness. The composition of an RBC determines its physical properties in polymerized form. In

173   this study, variations in the polymeric matrix and the filler concentration of new RBCs gave rise to

174   mechanical properties that could prove clinically advantageous over those of the conventional, gold-

175   standard RBCs that were tested. RBCs that are characterized by lower shrinkage and greater depth of

176   cure and by similar hardness at both the top and bottom surface could improve on the current bulk-

177   filling techniques.

178   Given that volumetric shrinkage is directly related to the organic matrix of the composite resin, it

179   was expected that SDR and silorane-based resins would shrink less than conventional methacrylate-

180   based RBC[12]. In addition, the amount of filler particles is related to polymerization shrinkage; non-

181   flowable RBCs, which have more filler than their flowable counterparts, typically shrink less during

182   polymerization than do flowable RBCs[3]. This emphasis on shrinkage is important; when high it may

183   contribute to a restoration's failure by affecting the marginal integrity, and possibly also lead to post-

184   operative sensitivity[17]. This study corroborates that volumetric shrinkage ascends for the tested

185   materials in the following order: silorane-based resin, non-flowable RBCs, and flowable RBCs.

186   Nevertheless, SDR presented values of volumetric shrinkage that were very similar to those of non-

187   flowable ones and significantly lower than those for other flowable RBC tested. Its inability to improve

188   on the non-flowable materials with respect to shrinkage may be due to the fact that the low contraction

189   of the resin monomer could not completely compensate for the lower percentage of filler (44%) in this

190   RBC.

191 Flowable RBCs typically have a greater depth of cure than their non-flowable counterparts. This is

192 because polymerization at depth is directly related to the filler's particle size and dispersion, with

193 smaller size and greater dispersion promoting differences in scattering of the light through the

194 material[14]. SDR presented statistically significant increase in depth of cure up to 3mm. This is an

195 improvement over all of the RBCs studied[20], though it is also less than the 4mm advertised by the

196 manufacturer[5]. However, other materials also failed to meet the depth-of-cure criteria (above 2mm

197 thickness). This may be due in part to the fact that depth of cure is influenced by RBC shade.

198 Knoop microhardness was used as a second method to assess the depth of cure in this study, based

199 on the discovery by Flury et al., in 2012[19] that for bulk-fill materials the ISO 4049 method

200 overestimated depth of cure compared to its determination by microhardness tests. The evaluation of

201 top and bottom KHN, and of the percentage reduction, revealed that the flowable RBCs generally

202 produced lower levels of microhardness at the top. The exception was SDR, whose top KHN was

203 significantly higher. Regarding bottom-surface KHN, SDR had the highest mean values, regardless of

204 viscosity, among the materials evaluated in this study. Notably, the ratio of the KHN at the top vs.

205 bottom of the specimen was the lowest in the case of SDR. This fact could be related to the higher

206 depth of cure obtained in the present study.

207

208 **CONCLUSIONS**

209 The following conclusions may be drawn:

210 1- The silorane-based resin (FP90) performed as observed in previous studies, exhibiting the least

211 polymerization shrinkage among the RBCs tested here.

212 **2-** The low shrinkage flowable composite (SDR) performed similarly to non-flowable with

213 significant difference compared to the other flowable RBCs.

214   **3-** All materials tested presented statistical significant differences for microhardness from the top

215   and from the bottom.

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Table 1(on next page)

Materials used in this study

Table 1 – Materials used in this study

Material Type/ Commercial name	Type	Matrix type	Photoinitiator system	Filler type	Filler loading (vol%)	Shade	Manufacturer	Batch #
Mycro-hybrid SureFil® SDR™Flow (SDR)	F, L	Polymerization modulator, dimethacrylate resins, UDMA	CQ	Ba-B-F-Al silicate glass, SiO2, Sr–Al silicate glass, TiO2	44	U	Dentsply	91130
Mycro-hybrid Tetric N Flow (TNF)	F	Bis-GMA, Bis-EMA, UDMA, TEGDMA	CQ	Barium glass, ytterbium trifluoride, Ba-Al-fluorosilicate glass, SiO2	39	A₂	Ivoclar /Vivadent	L40758
Nanofilled Filtek Z350 Flow (FZ350F)	F	Bis-GMA, Bis-EMA, TEGDMA	CQ	Agregated zirconia/silica cluster	55	A₂	3M Espe	1027100529
Mycro-hybrid Esthet-X HD (EXHD)	C	Bis-GMA, Bis-EMA, TEGDMA	CQ	Barium fluoroborosilicate glass and silica	60	A₂	Dentsply	L58656
Mycro-hybrid Tetric N Ceram (TNC)	C	Bis-GMA, Bis-EMA, UDMA	CQ	Barium glass, ytterbium trifluoride, Ba-Al-fluorosilicate glass, SiO2	55-57	A₂	Ivoclar /Vivadent	026700190
Nanofilled Filtek Z350 XT (FZ350)	C	Bis-GMA, Bis-EMA, UDMA, TEGDMA	CQ	Agregated zirconia/silica cluster	63.3	A₂E	3M Espe	1026600561

2	==Mycro==-hybrid							
3	Filtek P90 (FP90)	C, L	3,4-Epoxycyclohexyl ethylcyclopolyme thylsiloxane,	CQ, iodonium salt and electron donor	Silanized quartz; yttriumfluoride	55	A₂	3M Espe	3480370
4									

F: flowable; C: conventional; L: low-contraction; Bis-GMA: bisphenol-glycidyl-methacrylate; Bis-EMA: bisphenol-a-ethoxydimethacrylate; UDMA: urethane-dimethacrylate; TEGDMA: triethyleneglycoldimethacrylate; HEMA: hydroxyethylmethacrylate; CQ: camphorquinone.

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Table 2(on next page)

Arithmetical mean values of all tests (SD)

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Table 2 – Arithmetical mean values of all tests (SD)					
Material (n=10)	**Degree of polymerization shrinkage (%)**	**Depth of cure (mm)**	**Knoop microhardness (KHN)**		
			Top	**Bottom**	**Reduction (%)**
SDR	2.906 (0.04)^E	3.071 (0.05)^C	72.725 (1.24)^D	64.810 (0.04)^G	10.37
TNF	4.217 (0.08)^G	2.893 (0.07)^B	55.599 (0.02)^B	41.858 (0.55)^A	24.64
FZ350F	4.112 (0.05)^F	2.837 (0.13)^B	53.712 (1.32)^A	45.124 (0.16)^B	14.09
EXHD	2.256 (0.09)^D	2.612 (0.10)^A	77.422 (1.25)^F	61.321 (0.53)^D	21.01
TNC	2.031 (0.13)^B	2.544 (0.23)^A	64.130 (1.15)^C	52.029 (0.44)^C	18.62
FZ350	2.134 (0.07)^C	2.567 (0.13)^A	78.664 (0.68)^G	63.282 (0.81)^F	19.89
FP90	1.015 (0.12)^A	2.679 (0.06)^A	73.704 (0.61)^E	62.620 (0.69)^E	14.98
Values in each column represent the means and standard deviation (in parentheses). Upper-case letters in superscript designate groups whose p values for a given parameter (polymerization shrinkage, depth of cure or KHN) were not statistically different (p>0.05).					

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