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Effect of nanofiller fractions and temperature on polymerization shrinkage on glass fiber reinforced filling material

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ABSTRACT

Objectives. The aim was to evaluate the effect of different nanofiller fractions and temperature on polymerization shrinkage strain and degree of monomer conversion of short glass fibers reinforced semi-interpenetrating polymer network (semi-IPN)-polymer matrix composite resin.

Methods. Experimental composite resin was prepared by mixing 22.5 wt% of short E-glass fibers (3 mm in length) to the 22.5 wt% of resin matrix with various weight fractions of nanofillers (0, 10, 20, 30, 40, 50 wt%) and then 55 wt% of silane treated silica filler were added gradually using high speed mixing machine. Another study group contained composite resin prepared by mixing 22.5 wt% of resin matrix (without nanofillers) to 77.5 wt% of filler particles (without fiber fillers). As control material, commercial particulate filler composite resin was used. The shrinkage strain of the specimens was measured using the bonded-disk technique at 26 and 37 °C with respect to time. Degree of conversion of the experimental composites containing different nanofiller fractions was measured using FTIR spectroscopy.

Results. ANOVA revealed that fraction of nanofillers and polymerization temperature had significant effect ($p < 0.05$) on the shrinkage strain and degree of conversion of the composite resin. Shrinkage strain correlated with nanofiller fraction and polymerization temperature ($r^2 = 0.96$ and 0.95).

Significance. The use of high nanofiller fraction with short fiber fillers and IPN-polymer matrix yielded improved rate of shrinkage strain.

1. Introduction

Dental restorative filling composite resins have been introduced to dental community in 1960s [1]. Since then, after many significant material improvements, restorative composite resins still suffer from two key shortcomings: deficiencies of mechanical strength and high polymerization shrinkage [2]. Thus, advanced research have been undertaken to evaluate and improve composite resin in order to have a material with high strength and low polymerization shrinkage combined with advantages of esthetic properties. Attempts have been made to change the type of fillers or filler size and their surface silanization. By changing the polymerization kinetics of resins matrices and degree of monomer conversion has

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tried to be influenced [3–6]. Reinforcing the resin with glass fibers [7–9], with fiber-reinforced composite (FRC) substructure [10], whiskers [11], particulate ceramic fillers (dense and porous) [12] and optimization of filler content [3] are among the methods that have been studied. However, further significant improvements are still needed. The linear shrinkage of current composite resin ranged from 2 to 3% after curing [13]. Such shrinkage causes gaps to lead to secondary carries, which is a major problem in current restorative dentistry. Many factors affect the shrinkage of composites resins, including resin matrix composition, filler content, and polymerization method [14–16]. Filler technology has led to the development of composite resins characterized by containing zirconia or silica nanoparticle fillers of approximately 25 nm size and nanoaggregates of approximately 75 nm size.

Glass fibers have been investigated to reinforce dental polymers for over 30 years [17]. They have documented reinforcing efficiency and good esthetic qualities compared to carbon or aramid fibers [18–20]. The effectiveness of fiber reinforcement is dependent on many variables, including the resins used, the quantity of fibers in the resin matrix [21,22], length of fibers [22], form of fibers [23], orientation of fibers [24], adhesion of fibers to the polymer matrix [25], and impregnation of fibers with the resin [26]. Short random fibers provide an isotropic reinforcement effect in multidirections instead of one or two directions, as described by Krenchel [27].

Polymethyl methacrylate (PMMA) based semi-interpenetrating polymer network (semi-IPN) matrix has been established as a polymer matrix in denture base materials [28]. Also some products of fiber-reinforced composite use semi-IPN-polymer matrix [29]. However, dental restorative composite resins with semi-IPN-polymer matrix in combination with short glass fibers and particulate nanofillers have not been evaluated to the author's knowledge.

Therefore, the objective of the study was to provide an experimental material, which combines glass fiber, semi-IPN and nanofiller technologies.

Specifically, this study investigated the effect of nanofiller fraction and temperature on polymerization shrinkage on glass fiber reinforced filling material.

2. Materials and methods

2.1. Materials

Dimethacrylate (BisGMA 67% [bisphenol A-glycidyl dimethacrylate] and TEGDMA 33% [triethylenglycol dimethacrylate]) resin consisting nanofillers (SiO_2, 20 nm in size) with various weight fractions (Hanse Chemie, Germany) (Table 1) and E-glass fibers with BisGMA-PMMA [polymethylmethacrylate, Mw 220,000]) resin matrix (everStick, StickTech Ltd., Turku, Finland). In addition, radio-opacity fillers of $BaAlSiO_2$ ($3 \pm 2\,\mu m$ in size) (Specialty Glass, USA) were incorporated to the resin system. Before the $BaAlSiO_2$ filler particles were incorporated into the resin matrix, they were silane treated using previously defined technique [30] Commercial particulate filler composite (Grandio Caps, VOCO, Germany) was used as a commercial control group.

2.2. Methods

Experimental fiber composites (FC) were prepared by mixing 22.5 wt% of short E-glass fibers (3 mm in length) to 22.5 wt% of resin matrix with various weight fractions of nanofillers (0, 10, 20, 30, 40, 50 wt%) and then 55 wt% of $BaAlSiO_2$-radio-opacity fillers were added gradually to the mixture). Classification of the test groups according to various filler content is given in Table 1. The mixing was carried by using high speed mixing machine for 5 min (SpeedMixer, DAC, Germany, 3500 rpm). The dimethacrylate based resin matrix consisting PMMA forms semi-IPN-polymer matrix for the composite of FC. Experimental control group of particulate filler composite resin was prepared by mixing 22.5 wt% of dimethacrylate resin (with 50 wt% nanofillers) to 77.5 wt% of silane treated $BaAlSiO_2$-fillers. Commercial particulate filler composite (Grandio) was used as a commercial control group. All groups used in this study are listed in Table 1.

The shrinkage strain was measured at two different temperatures (26 and 37 °C) using the Watt's bonded-disk technique [31] (Fig. 1). The specimens from each group ($n = 5$) were photo-polymerized for 40 s using a light source with an irradiance of 550 mW/cm^2 (Optilux-500, Kerr, CT, USA) and the shrinkage strain data was recorded with respect a time (1 h).

Table 1 – Classification of test groups used in the study according to their filler content and composition ($n = 5$, per group)

Groups	Fibers (wt%)	Nanofillers (wt%) in the resin matrix/resin matrix (22.5 wt%)	Micrometer scale fillers (wt% of the resin–nanofiller–fiber mixture)
A (control)	–	–	77.5
B	0	0/22.5	77.5
C0	22.5	0/22.5	55
C1	22.5	10/22.5	55
C2	22.5	20/22.5	55
C3	22.5	30/22.5	55
C4	22.5	40/22.5	55
C5	22.5	50/22.5	55

0: No fibers, no nanofillers; A: commercial particulate filler composite (Grandio); B: experimental particulate filler composite; C: experimental fiber composite.

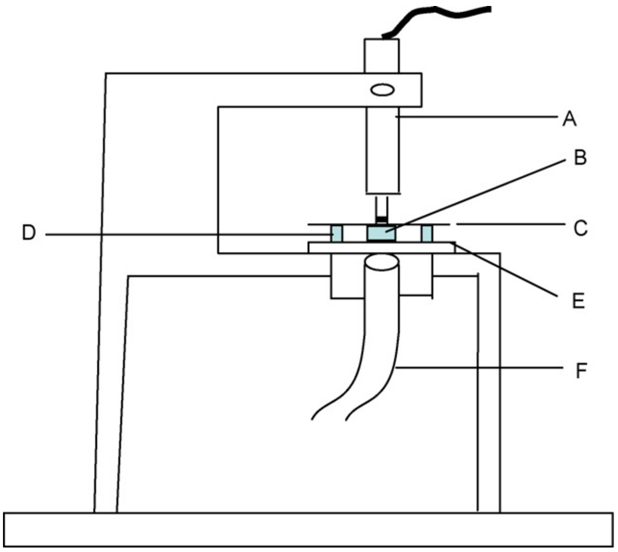

Fig. 1 – Schematic drawing of the cross-section of bonded-disk shrinkage measurement instrument: (A) LVDT transducer with 2 g probe mass; (B) disk specimen; (C) cover slip; (D) brass ring; (E) rigid glass plate; (F) light source.

The degree of monomer conversion (DC%) of test groups ($n = 5$/group) was monitored during polymerization by FTIR-reaction kinetics program (Time base-Spectrum One, Perkin-Elmer, Beaconsfield Bucks, UK) with an attenuated total reflectance (ATR) sampling accessory. Tested composite was placed in 1.8 mm-thick ring molds having diameter of 6.5 mm on the ATR-sensor (ZnSe-crystal). The upper surface of the specimen was covered with a Mylar sheet and a glass slide of 1 mm thickness and slightly pressed against the ATR to ensure the good contact of the specimen. The light source was placed in contact with glass surface. The substrate was light polymerized with a hand-held light-curing unit (Freelight 2, 3M ESPE, Elipar, Germany) for 40 s. The spectra during the polymerization process was recorded every 30 s until 15 min. The DC% was calculated from the aliphatic C=C peak at 1638 cm^{-1} and normalized against the aromatic C=C peak at 1608 cm^{-1} according to a formula (1)

$$\text{DC\%} = \left[1 - \frac{C_{\text{aliphatic}}/C_{\text{aromatic}}}{U_{\text{aliphatic}}/U_{\text{aromatic}}}\right] \times 100\% \tag{1}$$

where $C_{\text{aliphatic}}$ is the absorption peak at 1638 cm^{-1} of the cured specimen, C_{aromtic} the absorption peak at 1608 cm^{-1} of the cured specimen, $U_{\text{aliphatic}}$ absorption peak at 1638 cm^{-1} of the uncured specimen and U_{aromatic} is the absorption peak at 1608 cm^{-1} of the uncured specimen.

The fraction of remaining double bonds for each spectrum was determined by standard baseline techniques using the comparison of maximum heights of aliphatic and reference peaks for calculations.

Data of shrinkage strain measurements and degree of monomer conversions were statistically analyzed with analysis of variance (ANOVA) at the $p < 0.05$ significance level with SPSS (version 13, Statistical Package for Social Science, SPSS Inc., Chicago, IL, USA) to determine the differences between the groups.

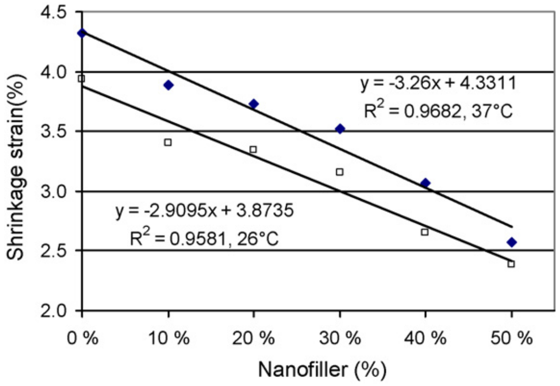

Fig. 2 – Linear regression ($n = 60$) between different weight fractions of nanofillers and shrinkage strain of test specimens. Upper line refers to measurement at +37 °C and lower line at +26 °C.

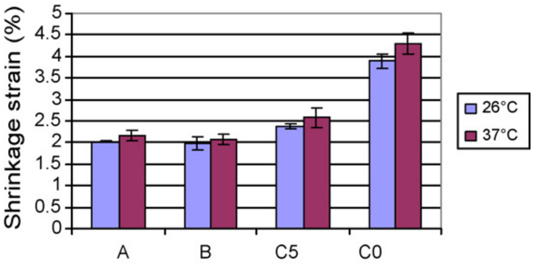

Fig. 3 – Polymerization shrinkage strain of tested groups (Table 1) measured at 37 and 26 °C. Vertical lines represent standard deviations.

3. Results

The mean values of shrinkage strain at different temperatures of tested groups with standard deviations (S.D.) are summarized in Figs. 2 and 3. ANOVA revealed that both nanofiller fraction and the polymerization temperature had a significant effect ($p < 0.05$) on the shrinkage strain. No significant difference in the shrinkage strain was found between experimental FC composite having 50 wt% nanofillers (group C5) and group A (control) and B ($p > 0.05$) (Fig. 3). Regression analysis revealed linear relationship between shrinkage strain and nanofiller fraction in both polymerization temperatures ($r^2 = 0.96$ and 0.95) (Fig. 2). Degree of monomer conversion after 15 min of photo-polymerization (40 s) showed significant difference between groups with different nanofiller fractions ($p < 0.05$) (Fig. 4). Experimental FC composite with 50 wt% nanofillers has lower degree of monomer conversion (50%) than group A (53%) and B (53%) (Fig. 5).

4. Discussion

This study revealed the effect of particulate nanofillers added to short glass FRC on the polymerization shrinkage strain

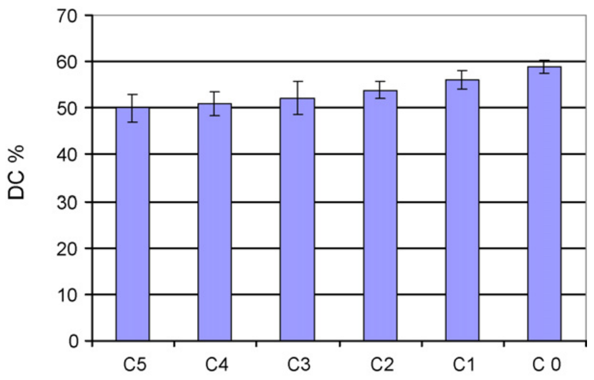

Fig. 4 – The degree of monomer conversion (DC%) of tested groups with different weight fractions of nanofillers polymerized with light-curing unit for 40 s at room temperature.

of composite resin. The data showed that the polymerization shrinkage strain decreased by increasing quantity of nanofillers. Incorporating nanofillers into composite resin reduced the fraction of shrinkable monomers leading to decreased polymerization shrinkage. The results indicated that the decrease in shrinkage was linearly related to the quantity of nanofillers (Fig. 2). As apparent in Fig. 4, there was proportional significant difference between the monomer conversion of the composites containing different quantities of nanofillers ($p < 0.05$). Our results are in agreement with Halvorson et al. [32] study, which found that conversion progressively decreased with increasing the filler loading because the mobility of resin-monomers was restricted due to existence fillers. This lead to decreased molecular and radical mobility and resulted lower monomer conversion. Unidirectional fiber-reinforced composites as an anisotropic material have negligible shrinkage strain in the direction of fibers compared to the isotropic particulate composite resins [33]. Different methods had been used to measure the polymerization shrinkage of resin-based materials including dilatometry, strain gages, dynamic mechanical analysis, linear displacement and bonded-disk methods [34,35]. Previously, it was shown that different techniques gave significantly different shrinkage strain values. Bonded-disk technique was introduced and analyzed in detail by Watts and Cash [31]. Bonded-disk technique measures axial-shrinkage (vertical direction), but with the disk-shape geometry of the sample, which is bonded on one side to a rigid glass surface, the value obtained is close to volumetric shrinkage, to a good approximation [36]. However, this occurs only with isotropic materials, like composite resin or short, random FRC having no specific filler orientation in their structure. When bonded-disk method is used to measure polymerization shrinkage, the fibers of the FC composite resin are oriented from original 3-D random orientation to 2-D random orientation, which changes anisotropic properties of the composite being transversally oriented to measurement axis. Thus, the effect of fibers on the polymerization shrinkage strain using bonded-disk technique was not able to be observed. Previous study by Tezvergil et al. [33] showed that fiber orientation is an important factor influencing the shrinkage strain and that the shrinkage strain along the fiber direction is low. Of the tested groups, the other study groups of particulate composite resin without fibers (group A and B) showed lowest shrinkage strain values. On the other hand, FC composite with 0% nanofillers (group C0) showed the highest shrinkage strain values (Fig. 3). Even though the total amount of fillers by wt% in both groups were same (Table 1). This is another aspect that can be explained due to the difference in fiber (2.54 g/cm^3) and particulate filler (1.5 g/cm^3) density. Therefore, the total filler volume fractions in particulate composite resin specimens in group A and B were higher than FC composite with 0% nanofillers (group C0). Fig. 3 shows that there was no significance difference between particulate filler composite (group A and B) and experimental FC composite with 50% nanofillers (group C5). From the clinical point of view, it is very important to know the effect of temperature on the polymerization shrinkage strain. It was concluded that polymerization shrinkage strain increased with increasing temperature (Fig. 2), which can be explained by higher monomer conversion at elevated temperature shown in previous studies [14].

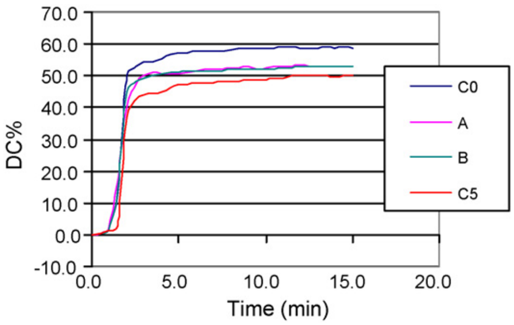

Fig. 5 – The degree of monomer conversion (DC%) of tested groups (Table 1) polymerized with light-curing unit for 40 s.

The authors hypothesize that the use of short fiber fillers could reduce the shrinkage and shrinkage stress of the composite and the question will be evaluated in further studies.

It was concluded that addition of particulate nanofillers to short glass fiber reinforced composite yielded improved rate of polymerization shrinkage strain.

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