Creep of experimental short fiber-reinforced composite resin

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The purpose of this study was to investigate the reinforcing effect of short E-glass fiber fillers oriented in different directions on composite resin under static and dynamic loading. Experimental short fiber-reinforced composite resin (FC) was prepared by mixing 22.5 wt% of short E-glass fibers, 22.5 wt% of resin, and 55 wt% of silane-treated silica fillers. Three groups of specimens ($n=5$) were tested: FC with isotropic fiber orientation, FC with anisotropic fiber orientation, and particulate-filled composite resin (PFC) as a control. Time-dependent creep and recovery were recorded. ANOVA revealed that after secondary curing in a vacuum oven and after storage in dry condition for 30 days, FC with isotropic fiber orientation (1.73%) exhibited significantly lower static creep value ($p<0.05$) than PFC (2.54%). For the different curing methods and storage conditions evaluated in this study, FC achieved acceptable static and dynamic creep values when compared to PFC.

Keywords: Composite resin, Experimental fiber-reinforced composite, Creep

INTRODUCTION

Resin composites were found to be lacking in durability for routine use in high stress-bearing applications^{1,2}. Attempts to improve the mechanical properties and load-bearing capacity of resin composites included changing the type or size of fillers, use of surface silanization^{3,4}, reinforcing the resin with glass fibers⁵⁻⁷, whiskers⁸ or particulate ceramic fillers⁹, or by filler content optimization⁹.

On fiber reinforcement, glass fibers are lauded for their reinforcing efficiency in improving impact strength and for their excellent esthetic qualities¹⁰. Nonetheless, fiber reinforcement effectiveness depends on a slew of factors: quantity of fibers in the resin matrix^{11,12}, length of fibers¹², form of fibers (*i.e.*, chopped *versus* continuous)¹³, orientation of fibers¹⁴, quality of adhesion between fibers and the polymer matrix¹⁵, and impregnation of fibers with resin¹⁶.

Fiber pre-impregnation can be carried out with different types of monomer resins, such as dimethacrylate, trimethacrylate, or dendrimer. However, it has been shown that pre-impregnation of fibers with a light-polymerizable dimethacrylate resin system containing linear polymer phases is critical to improving the interfacial adhesion of fiber-reinforced composite (FRC) appliances to composite resins. This is because dimethacrylate monomers form a semi-interpenetrating polymer network (semi-IPN) with linear polymer phases by polymerization, providing better bonding sites for composite resins^{11,15}. As for the effects of fiber length, fiber form, and fiber orientation upon reinforcement,

Krenchel reported that short, chopped fibers which were randomly oriented provided isotropic reinforcement in multiple directions, as opposed to only one or two directions¹⁷. It was also favorably reported that when short E-glass fibers were combined with semi-IPN polymer matrix in restorative filling composite resins, there were marked improvements in mechanical properties and load-bearing capacity¹⁸⁻²¹.

Despite the introduction of reinforcement to composite resins, there is a need to understand the relationship between material performance and deformation behavior when under applied stress. The normal deformation response of polymer materials can be studied by measuring the strain generated during a specified period of appropriate constant stress application (*i.e.*, static creep), followed by removal of stress and measurement of the subsequent relaxation response of the material (*i.e.*, recovery) over a selected duration. For dental restorations, the stress encountered under normal conditions is low in magnitude, high in frequency, and for a short duration. It was estimated that the chewing frequency encountered by a dental restoration in the human mouth is more than 3×10^5 times per year²². In the context of dental restorations, it is therefore important to investigate the relationship between material performance and deformation behavior under cyclic stress (dynamic creep).

The aim of this study was to evaluate the creep values of experimental, short glass fiber composite resins which were cured using different methods and stored under different conditions at a constant temperature. The hypothesis of this study was that isotropic short-

fiber fillers could reduce the creep value of composite resins.

MATERIALS AND METHODS

Materials

Materials used in this study are listed in Table 1. The dimethacrylate resin matrix (Bis-GMA 67 wt% [bisphenol A-glycidyl dimethacrylate], TEGDMA 32.3 wt% [triethylene glycol dimethacrylate], CQ and DMAEMA 0.7 wt% [camphorquinone and dimethylaminoethyl methacrylate]) consisted of 50 wt% of SiO₂ nanofiller (Hanse Chemie, Germany; particle size=20 nm). Reinforcement material was everStick fibers (Stick Tech Ltd., Turku, Finland), which were E-glass fibers pre-impregnated with Bis-GMA and PMMA [poly(methyl methacrylate); M_w=220.000].

Experimental short fiber composite resin (FC) was prepared by mixing 22.5 wt% of short E-glass fibers (3 mm in length) to 22.5 wt% of dimethacrylate resin matrix. Then, 55 wt% of BaAlSiO₂ radio-opacity particulate fillers (Specialty Glass, USA; 3±2 µm in size), which were silane-treated²³⁾, were gradually added to the mixture. Mixing was performed using a high-speed mixing machine (SpeedMixer, DAC, Germany; 3500 rpm) for 5 min. Therefore, the FC composite resin was a dimethacrylate-based resin matrix containing PMMA linear polymer phase, such that a semi-IPN polymer matrix would be formed by polymerization.

For control, a commercial particulate-filled composite resin, Z250 (3M ESPE, USA; Bis-GMA, UDMA, Bis-EMA, 79 wt% filler) of shade A2, was used.

Experimental groups

Solid cylindrical specimens (4×6 mm), according to each experimental group's composition, were prepared using split steel molds. There were three experimental groups (*n*=5) in this study as follows:

Group A: FC composite resin with isotropic fiber orientation (3D fiber orientation: fibers oriented into two horizontal directions and one vertical direction);

Group B: FC composite resin with anisotropic fiber orientation (2D fiber orientation: fibers

oriented into two horizontal directions); and

Group C: Commercial particulate-filled composite resin (PFC).

Specimens were cured using one of these methods: (1) Polymerization by handheld light curing unit (LCU) with an irradiance of 550 mW/cm² (Optilux 500, Kerr, CT, USA) for 80 s from both top and bottom surfaces; or (2) Secondary curing in a visible light curing (VLC) vacuum oven (Visio Beta, ESPE, Germany) for 15 min. Cured specimens were either dry-stored or water-stored at a constant temperature (37°C) for 30 days until creep testing.

Static and dynamic creep tests

For the static creep test, specimen was placed in a loading device (Fig. 1) and subjected to a constant stress of 20 MPa for 2 h, followed by 2 h of strain recovery after load removal. During the entire loading and unloading time, applied load was monitored and deformation was measured as per described in previous studies²⁴⁻²⁶⁾.

For the dynamic creep test, a universal testing machine (Z020, Zwick/Roell GmbH & Co. KG, Ulm, Germany) was used. Loading cycles of 4 s each were accomplished repeatedly and reliably according to the preset test parameters for load amplitude and load

Fig. 1 Loading device for static creep test.

Table 1 Materials used in this study

Composite resin	Manufacturer	Lot number	Composition
Z250	3M ESPE, St. Paul, MN, USA	20090707	Bis-GMA, UDMA, Bis-EMA
Short fiber composite, FC	Experimental	2100524-D7-022	Bis-GMA, TEGDMA
everStick	Stick Tech Ltd., Turku, Finland	2050426-ES-125	PMMA, Bis-GMA

PMMA: Poly(methylmethacrylate), M_w=220.000

Bis-GMA: Bisphenol-A-glycidyl dimethacrylate

TEGDMA: Triethylene glycol dimethacrylate

UDMA: Urethane dimethacrylate

Bis-EMA: Bisphenol-A-polyethylene glycol diether

duration. During each loading cycle, stress increased and then decreased between 1 MPa and 50 MPa at a constant rate. Load and displacement data as functions of time for 450 loading cycles were recorded within 30 min. Load was recorded in increments of 1 N, while increments of time and displacement were 0.01 s and 1 μ m respectively.

Load, displacement, and time data were processed using MATLAB R2007b software. Amongst the stress values recorded during the loading phase of each cycle, only the creep strain and time data corresponding to 35 and 36 MPa of stress were used for this study. An optimized plot of creep strain-*versus*-time was then obtained based on a quadratic regression analysis of the selected data. Average dynamic creep values for each time moment were calculated from the different experimental runs.

Statistical analysis

Statistical analysis was performed using SPSS version 10.0 (SPSS Inc., Chicago, IL, USA). Static and dynamic

creep data were statistically analyzed using analysis of variance (ANOVA) followed by Tukey's *post hoc* test at significance level of 0.05 to determine the differences among the groups. Types of composite, curing method, and storage condition (dry- or water-stored) were used as independent factors.

RESULTS

The mean and standard deviation values of static and dynamic creep strains of dry- and water-stored specimens are summarized in Tables 2a and 2b respectively.

In Table 2a for dry-stored specimens, ANOVA revealed that the static creep strain values of FC after secondary curing in vacuum oven (Group A: 1.73% and Group B: 2.07%) were significantly lower than PFC (2.54%) ($p < 0.05$). Indeed, secondary curing in a visible light curing oven (OLC) resulted in significantly lower static and dynamic creep values than curing with a handheld LCU (HLC) for Groups A to C. Curing with a handheld LCU or cyclic loading did not result

Table 2

(a) Mean and standard deviation values of time-dependent creep parameters of dry-stored specimens after secondary cure in visible light curing oven (OLC) and light-curing with handheld LCU (HLC)

Groups	Curing mode	Static creep strain %	Dynamic creep strain %
Group A	OLC	1.73 (0.33) ^a	1.16 (0.39) ^a
	HLC	3.78 (1.22) ^c	1.93 (0.12) ^b
Group B	OLC	2.07 (0.35) ^a	1.04 (0.19) ^a
	HLC	3.50 (1.31) ^c	1.88 (0.63) ^b
Group C	OLC	2.54 (1.05) ^b	1.13 (0.19) ^a
	HLC	3.10 (0.40) ^{b,c}	1.27 (0.28) ^{ab}

(b) Mean and standard deviation values of time-dependent creep parameters of water-stored specimens after secondary curing in visible light curing oven (OLC) and light-curing with handheld LCU (HLC)

Groups	Curing mode	Static creep strain %	Dynamic creep strain %
Group A	OLC	2.14 (0.44) ^a	1.63 (0.46) ^a
	HLC	3.48 (0.92) ^c	1.99 (0.64) ^a
Group B	OLC	3.07 (0.53) ^b	2.76 (0.88) ^b
	HLC	2.28 (0.85) ^a	1.35 (0.62) ^a
Group C	OLC	2.41 (0.39) ^a	1.23 (0.21) ^a
	HLC	2.18 (0.43) ^a	1.56 (0.28) ^a

Group A: Experimental FC composite resin with isotropic fiber orientation;

Group B: Experimental FC composite resin with anisotropic fiber orientation;

Group C: Commercial particulate-filled composite resin.

Same superscript letters indicate that data are not statistically different ($p > 0.05$).

in significant differences in both static and dynamic creep strain values among Groups A to C ($p>0.05$). For both curing methods, there were also no statistically significant differences ($p>0.05$) in both static and dynamic creep strain values between Groups A and B of different fiber orientations.

In Table 2b for water-stored specimens, ANOVA revealed that the influences of curing method (OLC) and storage condition (water storage) were higher in FC specimens than in PFC.

DISCUSSION

The creep-recovery profiles of the resin composites investigated in this study followed the typical stages of deformation and recovery generally observed for polymeric materials²⁴. Therefore, the time-dependent creep deformation and recovery measurement method used in this study provided an insight not only into the material's ability to resist stresses without catastrophic failure, but also how stresses were accommodated by compliance through viscoelastic behavior and viscous fluidity when under constant dynamic loading, and the degree to which the material would relax towards its original configuration when the load was removed^{25,26}.

Effect of fiber length

It was favorably reported that the use of short glass fibers with a semi-IPN matrix in restorative filling composite resins resulted in improved mechanical properties, load-bearing capacity, and polymerization shrinkage^{18–21}. For this reason, the hypothesis of this study was that short E-glass fiber fillers with a semi-IPN resin matrix could reduce the creep value of composite resins.

The reinforcing effect of fiber fillers is due to stress transfer from polymer matrix to fibers, when the fiber length is equal to or greater than the critical fiber length^{5,18}. It was established through a fiber fragmentation test that the critical fiber length of E-glass with Bis-GMA polymer matrix ranged between 0.5 and 1.6 mm⁵. Based on this finding⁵, fiber fillers of 3 mm length were used in this study.

Effect of fiber orientation

According to Krenchel¹⁷, short random-orientated fibers in 3D orientation gave a strengthening factor of 0.2, whereas fibers in 2D orientation gave 0.38 and unidirectional fibers a factor of 1. However, in this study, there were no statistically significant differences in creep deformation response between Groups A and B with different fiber orientations.

The creep measurement apparatus (Fig. 1) used in this study measured surface deformation. Specimens used in this study had a cylindrical geometry, and when specimen was bonded on both sides to rigid surfaces, the creep value obtained only closely approximated deformation in the vertical direction.

Split steel mold was used to prepare the specimens in this study. As a result, fibers of the FC composite resin were re-oriented from the original 3D random

orientation to a 2D orientation. The composite then had anisotropic properties as fibers were transversely oriented to the measurement axis. Consequently, the effect of different fiber orientations on creep behavior could not be thoroughly observed using the creep measurement apparatus in this study. A previous study by Tezvergil *et al.* showed that fiber orientation was an important influencing factor on polymerization shrinkage strain in that shrinkage strain was low along the fiber direction²⁷.

For the particulate-filled composite resin (PFC) without fibers (*i.e.*, Group C), there were no significant differences in both static and dynamic creep values between HLC and OLC for both storage conditions (dry and wet). This occurred only with isotropic materials. In the case of PFC, it was a composite resin with no specific filler orientation in its structure and hence behaved like an isotropic material. Filler density also contributed to this result. Fiber density was 2.54 g/cm³ while that of particulate filler was 1.5 g/cm³. As a result, the total filler volume fraction in PFC was higher than the FC specimens, and hence improved mechanical and creep properties in PFC than in FC specimens.

Effect of curing method

Experimental short fiber-reinforced composite resins (Groups A and B) stored under dry condition exhibited significantly lower ($p<0.05$) creep values than conventional composite resin PFC—but only after secondary curing and under static loading (Table 2a). This could be explained by the lower depth of cure in experimental short fiber composite resins than the conventional composite resin²⁸. However, exposure in a visible light curing oven resulted in a more homogeneous polymer matrix with a lower content of residual monomers. Differences in filler and polymer matrix types also contributed to the results of this study. A semi-IPN matrix lowers the crosslinking density of the resin matrix, which then led to an increase in the creep of the experimental short fiber-reinforced composite resins. Nonetheless, both types of materials met the requirements for clinical use^{24,25,29}.

According to Kildal and Ruyter, the curing method and water sorption behavior influenced the creep of composite resins³⁰. Results of this study concurred that the curing method affected the effect of water absorption on the static and dynamic creep behaviors of both FC and PFC composites, especially in the case of FC composites. It was found that up to 0.4–1.21 wt% of the original weight of unpolymerized Bis-GMA monomers remained in the light-cured polymer after curing and which were prone to leach, although the large molecular size of the Bis-GMA monomers hindered their diffusion from the crosslinked matrix³¹. In the present study, a short curing time with a handheld LCU (HLC) resulted in more residual unpolymerized monomers, which probably leached out from the cured materials in a wet environment and were replaced by water. A higher moisture content would have a plasticizing effect, thus resulting in higher creep.

In contrast, a longer curing time in a light curing oven resulted in less residual monomers. This meant reduced leaching of uncured monomers, and hence reduced plasticizing effect of water on the cured material. In the present study, OLC curing method significantly ($p=0.01$) decreased the creep values.

CONCLUSIONS

Within the limitations of the current study, the following conclusions were drawn:

1. Short E-glass fiber resin composite with semi-IPN polymer matrix achieved acceptable static and dynamic creep values when compared to conventional particulate-filled composite resin.
2. For both short fiber-reinforced and particulate-filled composite resins, their creep behavior could be improved by increasing the curing time and by storing the cured materials in a dry condition to avoid moisture absorption during storage and hence compromised creep properties.

The creep properties of a composite resin are not useful in predicting its abrasiveness against human enamel. On wear, abrasion and attrition, aging processes such as alternate thermal stress and wear should be considered to simulate the challenging clinical conditions which composite resins encounter in the human mouth. Therefore, the *in vitro* wear of short glass fiber composite resin with semi-IPN polymer matrix will be evaluated in future studies.

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