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Flexural properties of *experimental* nanofiber reinforced composite are affected by resin composition and nanofiber/resin ratio

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ARTICLE INFO

Article history:
Received 6 November 2014
Received in revised form 7 May 2015
Accepted 25 June 2015

Keywords:
Nanofibers
Electrospinning
Polyacrylonitrile
Resin composite
Flexural properties

ABSTRACT

Objectives. To evaluate the influence of different resin blends concentrations and nanofibers mass ratio on flexural properties of experimental Poliacrylonitrile (PAN) nanofibers reinforced composites.

Materials and methods. Poliacrylonitrile (PAN) nanofibers mats were produced by electrospinning and characterized by tensile testing and scanning electron microscopy (SEM). Experimental resin-fiber composite beams were manufactured by infiltrating PAN nanofiber mats with varied concentrations of BisGMA–TEGDMA resin blends (BisGMA/TEGDMA: 30/70, 50/50 and 70/30 weight%). The mass ratio of fiber to resin varied from 0% to 8%. Beams were cured and stored in water at 37 °C. Flexural strength (FS), flexural modulus (FM) and work of fracture (WF) were evaluated by three-point bending test after 24 h storage.

Results. The tensile properties of the PAN nanofibers indicated an anisotropic behavior being always higher when tested in a direction perpendicular to the rotation of the collector drum. Except for WF, the other flexural properties (FS and FM) were always higher as the ratio of BisGMA to TEGDMA increased in the neat resin beams. The addition of different ratios of PAN fibers did not affect FS and FM of the composite beams as compared to neat resin beams ($p > 0.05$). However, the addition of fibers significantly increased the WF of the composite beams, and this was more evident for the blends with higher TEGDMA ratios ($p < 0.05$).

Significance. The inclusion of PAN nanofibers into resin blends did not negatively affect the properties of the composite and resulted in an increase in toughness that is a desirable property for a candidate material for prosthodontics application.

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http://dx.doi.org/10.1016/j.dental.2015.06.018

1. Introduction

Resin composites materials have been used in dentistry for more than 50 years, mainly as direct restorative materials. However, no major changes had occurred on the material design since its introduction in clinical use. The vast majority of dental restorative resin composites available today are classified as particulate composites. They usually consist of ceramic-based particles with sizes ranging from 5 nm to 50 μm surrounded by a light curable methacrylate matrix. Monomers solutions typically used are blends of bisphenyl-glycidyl-dimethacrylate (BisGMA) and triethyleneglycol-dimethacrylate (TEGDMA) [1]. The clinical performance of most direct composite restorations is acceptable. However, clinical success for large direct and indirect restorations is still controversial. Moreover, fracture is the one of the main reasons for clinical failure due to fatigue stresses developed in function [2].

In engineering, electrospinning has emerged as a suitable technology for the production of polymer nanofibers [3]. It consists in generating a high voltage between a negatively charged polymer solution inside a syringe feeder and a positively charged metallic collector. The resulting electrostatic force induces the elongation of the polymer solution and the production of ultrafine fibers (nanometer scale) on top of the collector in the form of a randomly oriented fibrous mat with a large surface area to volume ratio [4].

It has being suggested that this extreme reduction in fibers size, i.e. diameters within the nanometer level, provides unique characteristics such as improvement of strength, modulus and toughness simultaneously. Indeed, a recent study showed that polyacrylonitrile (PAN) nanofibers with reduced diameter (ca. <200 nm) resulted in significant increase in strength and modulus at no expenses of the elongation at break, thus also resulting in a desirable increase in toughness [5]. Clearly, these unique characteristics of fiber production offer a promising insight for the development or improvement of fiber-reinforced dental composites.

Indeed, some efforts have being made to reinforce dental resin composites with nanofibers. The addition of electrospun nanofibers produced from nylon 6 [6] and polyacrylonitrile-polymethylmetacrylate (PAN-PMMA) [7] to methacrylate resin resulted, in general, in increased flexural properties of the composite. However, at some resin concentration and PAN fiber to polymer ratio the flexural properties decreased, and that was deemed to be due to limitations of the bonding between the fibers and the resin matrix [7]. In another effort, the addition of cellulose acetate nanofibers to resin resulted in decrease flexural strength, and that was due to incomplete wetting of the nanofibers by the infiltrating resin, thus resulting in air inclusion and voids that ultimately compromised the strength [8]. These findings suggest that the achievement of the desirable benefits of nanofiber reinforcement is limited by the ability of the resin to properly wet and penetrate the interfibrilar spaces of the fibrous mesh.

The role of the viscosity of the resin monomer solutions in the resultant characteristics and properties of traditional filled dental resin composite is well known [9,10]. Due to the different molecular structure of the monomers (e.g. higher molecular weight and less molecular mobility of BisGMA), increased viscosities result from increased concentrations of BisGMA. Low molecular weight monomers, such as TEGDMA, are usually added to the solutions to act as diluents and allow a suitable viscosity for the incorporation of the particle fillers [9]. Moreover, the lower flexibility of the BisGMA molecule and the presence of the hydroxyl groups, that can form hydrogen bonds, increase the rigidity of the polymer network [11]. Indeed, increasing concentrations of BisGMA result in increased flexural strength of experimental resin formulations [12] and resin composites [13]. Similarly, the resin viscosity also plays an important role on fiber reinforced composite processing. Wetting of fibers is more difficult with increasing resin viscosities since more viscous resins offer more resistance to flow and to penetrate the interfibrilar spaces [14]. Hence, resin viscosity can be related to the presence of voids and defects in the material that could compromise its mechanical properties and performance [15].

No effort has yet been made to investigate the role of methacrylate resin formulation and viscosity on the properties of nanofibers-reinforced composite. Thus, the objective of this study was to investigate the effect of BisGMA/TEGDMA ratio and resin blend to fiber mass ratio on the flexural properties of an experimental reinforced composite. The null hypotheses tested were that neither resin blend ratio nor nanofibers mass ratios would affect the flexural properties of the experimental nanofiber reinforced resin composite.

2. Methods and materials

2.1. *Production and characterization of the nanofibers*

2.1.1. *Electrospinning of PAN nanofibers*

PAN powder (Mw = 150,000 G/mol, Scientific Polymer Products, Ontario, NY, USA) and N,N-dymethylformamide (DMF) solvent (Fisher Scientific, Waltham, MA, USA) were purchased for the production of the nanofibers. Twenty grams solution was prepared by dissolving PAN powder in DMF solvent in a 7 wt% concentration of PAN. The solution was vigorously stirred overnight at room temperature. Electrospinning of PNA nanofibers was carried out in a custom-made electrospinning unit that consisted of a metallic rotatory collector drum covered with an aluminum foil and a syringe feeder system attached to a high-voltage power supply. The method is standard and has been described in details elsewhere [4]. This process forms a layer of nanofibers on the aluminum foil surface that will be referred hereafter as nanofiber mat. The spinning process was performed with applied voltage of 20 kV, distance of 17 cm between the needle tip and the collector and a flow rate of the solution of 0.01 ml/min. The collector drum had a circumference of 33 cm and rotated at 6.1 rpm. In this study, no attempt was made to align the jet with the use of secondary electro-voltage. Therefore, the unstable jet causes a whipping effect of the fiber and results in a random deposition of the fibers on the entire width of the collector drum. A total of 20 ml of solution was spun for 2 consecutive days. The formed fiber mat was removed from the collector drum and stored flat on the supporting aluminum foil until used.