

Nanocomposites for Restorative Dentistry

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ABSTRACT

In the present investigation a new method is described for modification of dental resins with reactive polymeric nanoparticles (RPNPs) as organofillers. Nanoparticles (NPs) as model compounds indicate clearly that the RPNPs significantly influence the mechanical and shrinkage properties of the matrix and composite. Nanoparticles were prepared by free radical non-linear copolymerization of a mixture of mono (styrene, ST) and bifunctional (ethylene glycol dimethacrylate, EGDM) comonomers in homogeneous solution. The EGDM monomer is a commonly used component of several dental filling composites. The size, reactivity and distribution of nanoparticles are influenced by the mole ratio of the monomers in the feed. Size of nanoparticles was determined by Scanning Electron Microscopy (SEM). Reactivity of nanoparticles was measured by Nuclear Magnetic Resonance (NMR).

Keywords: modified resin, dental composite, Reactive Polymeric Nanoparticles (RPNPs), photopolymerization

1 INTRODUCTION

Dental resin composites comprise a blend of hard, inorganic particles bound together by a soft, resin matrix. During the photopolymerization, the conversion of the monomer molecules of the matrix into a polymer network is accompanied by a closer packing of the molecules, which leads to bulk contraction. [1] Polymerization shrinkage of dental resin composites is due to the fact that monomers are converted into a polymer network and therefore exchanging van der Waals spaces in covalent bond spaces. This polymerization shrinkage creates contraction stress in the resin composite restoration and internal stress and deformation in the surrounding tooth structure [2,3]. Polymerization shrinkage is a critical limitation of dental composite resins. Stresses from shrinkage can cause clinical problems such as postoperative pain, fracture of the tooth, and opening of restoration margins that can result in microleakage and recurrent carries. [4-8] Many factors have a direct effect on the polymerization shrinkage of composite resin: curing method (chemical or light-curing),

placement technique (incremental or bulk), cavity configuration and size of the restoration.

Reduction of the polymerization shrinkage has been an important issue, since the use of dental resin composites. Non-shrinking resin and modified resin filler particles have been developed to tackle this problem, but are not commercially available yet. [9]

Polymerization shrinkage, contraction stress, elastic modulus [10], and flow are important factors determining the final properties of the resin composite. However, so far, only polymerization shrinkage is relation to elastic modulus, and polymerization contraction stress in relation to elastic modulus, and filler load and type of resin composite have been evaluated.

The present study is focused on the modification of resin by adding reactive polymeric nanoparticles. A number of reports describe the modification of materials by varying the parameters of filler materials (particle size and distribution of inorganic particles, concentration of inorganic filler in dental composite). Highly filled resin composites have low shrinkage values, high contraction stress values and are relatively ridged. The low-viscosity or flowable resin composites have high shrinkage values, low contraction stress values and are relatively flexible. It was expected that properties of modified resin will show lower shrinkage and their mechanical properties will be better, than the commercial dental materials. It has to build a unique material so the nanoparticles and the resin have to be compatible, nanoparticles have to dissolve or swell in the mixture of monomers.

2 EXPERIMENTAL SECTION

2.1 Materials

Mono and bifunctional monomers were used to prepare reactive polymeric nanoparticles. ST and EGDM monomers were purchased from Sigma-Aldrich. Azobis(isobutyronitrile) (AIBN, Sigma-Aldrich) was used as initiator and was recrystallized from methyl alcohol. The resin was a commercial material with filler content (60 w/w %). The organic resin portion was taken to perform measurements.

2.2 Characterization

Nuclear magnetic resonance spectroscopy (^1H NMR) Experiments were performed on Bruker 200 WP instrument at 200 MHz operating frequency in CDCl_3 solution at 10 mg/ml RPNPs concentration. The vinyl concentration was calculated by the integrations of peaks in the spectrum, and reactivates were compared for RPNPs obtained with different monomer feed.

Scanning electron microscopy (SEM) SEM micrographs were taken on SEM Hitachi 3000N instrument. In order to obtain good images of separated polymer particles, the samples were diluted in chloroform then mixed with 10 % v/v amount of MeOH until the solution turned opalescent. Subsequent to this 0.08 mol/dm^3 sodium-dodecil-sulfate (SDS) solution was added. The sample was placed on the cooper grid covered by coal layer. Solution was dried at room temperature and was covered by thin gold layer. The images were obtained at 25 and 30 kV and at different magnification factors. Size of NPs incorporated into a specimen was analysed.

The surface of fracture was covered by Au layer. The uniformity of nanocomposite was observed by SEM method.

Flexural Stress analysis (FS) Measurements were performed by an Instron 4302 testing instrument carried out by three-point loading. The crosshead speed was 0.5 mm/min. The data were calculated according to the International Standard Organization (EN ISO) Specification No. 178. Span was 18 mm between two supports.

Analysis of shrinkage Measurements were done using pycnometer, for resin, modified resin and commercial material. Materials were weighed into the pycnometers and filled by water. The pycnometer was placed in the photopolymerization lamp (blue light, $\lambda = 435 \text{ nm}$) for 30 minutes. After the photopolymerization the materials have shrunken and the volume contraction was calculated.

2.3 Formation

Synthesis of RPNPs

Nanoparticles were synthesized by free radical non-linear copolymerization in solution. [11,12] The solution was toluene and it was purified by distillation. Like in a typical copolymerization reaction, styrene (ST), ethylene glycol dimethacrylate (EGDM) and α, α' - azobis(isobutyronitrile) (AIBN) were heated to 60°C in homogeneous solutions (toluene), in which the concentration of the total amount of monomers was 0.556 mol/dm^3 . Samples were taken before the gelation process and then mixed with fourfold excess of methyl alcohol, and the copolymer precipitate was removed using an ultracentrifuge. The copolymers were then purified by dissolution in toluene followed by repeated precipitation with quadruple excess of methyl alcohol, and then samples were again centrifuged. This purification process was then repeated twice and completed by drying at ambient temperature in vacuum.

Modification of resin It is very important that the resin and reactive polymeric nanoparticles should be compatible. The RPNPs have to dissolve or swell in the resin and it has to build a unique in which the distribution of nanoparticles has to be homogenous. The weight ratio of resin and nanoparticles was 3:1. The nanoparticles were dissolved in toluene, and it was mixed to the resin. Then the solution was removed in vacuum (5-6 mbar, 25°C , 30 min). Shrinkage and mechanical properties of modified resin were measured.

Preparation of specimens for FS The specimens were prepared by a special specimen maker. Before the photopolymerization the shape was spread by silicone. A prismatic specimen was solidified by blue light photo polymerization. Parameters of specimen were 20 mm x 2 mm x 2 mm.

3 RESULTS AND DISCUSSION

3.1 Formation of reactive polymeric nanoparticles

Free radical copolymerization of ST and EGDM was performed in toluene. Well known non-linear polymerization results linear growing radicals with pendant vinyl groups in the first step. Propagation steps lead to the formation of side chains and loops. Loops are formed when the growing radical reacts with the pendant vinyl group sitting on the same polymer chain. Since the growing macromolecules permanently contain reactive pendant group further propagation and formation of cross-links continues.

3.2 Particles size by SEM

SEM micrographs provide visual evidence of the morphology and size of the dried copolymer nanoparticles. Figure 1 (A, B and C) represents the SEM micrographs of ST-EGDM copolymer prepared at 0.556 mol/dm^3 concentration of the total monomers with 5 mol% AIBN at 120 min of reaction time. The SEM photographs of copolymer particles show that their size ranges from around 50 nm to $1.5 \mu\text{m}$. As a consequence of the fractionalization resulting from the evaporation of the applied solvents the small copolymer nanoparticles tend to agglomerate, though individual nanoparticles can also be observed in Figure 5A and B. As shown in Figure 1 (C) the polymer cluster is composed of the aggregation of 50-100 nm sized spherical particles.

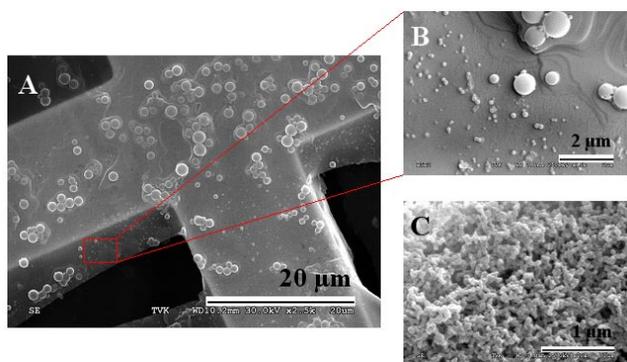


Figure 1: SEM micrograph of ST/EGDM copolymer prepared at 0.556 mol/dm^3 concentration of the total monomers with 5 mol% AIBN at 120 min of the reaction time.

3.3 ^1H NMR measurements of nanoparticles

A typical ^1H NMR spectrum of the region from 0.0 to 8.5 ppm is shown in Figure 2. In the present work the pendant vinyl group content of ST-EGDM copolymers was measured by ^1H NMR. The integral values of the corresponding peaks in the ^1H NMR spectrum, namely that of the vinyl hydrogens between 5.4 - 5.7 ppm and 5.9 - 6.3 ppm and the $-(\text{CH}_2)_2-$ unit in EGDM between 3.6 and 4.6 ppm, were used to calculate the ratio of the pendant double bonds of the copolymers.

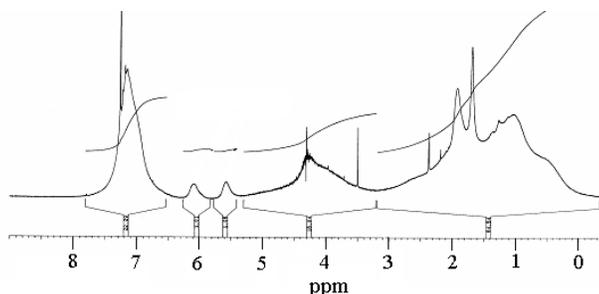


Figure 2: ^1H NMR spectrum of a ST/EGDM copolymer sample in CDCl_3 (ST/EGDM = 5/5, reaction time 120 min, 5 mol% AIBN).

3.4 Flexural Stress analysis

Mechanical properties are shown in Figure 3. According curves it is shown that the load-displacement curves of modified resin are between curves of the commercial and unfilled commercial materials. The results clearly show that the slope of modified resin is higher than that of the unfilled commercial material. It means that the modified resin has advanced mechanical properties than the unfilled commercial material. Moreover, the elasticity of these materials is similar (In the both cases the maximum displacement is about 2 mm.)

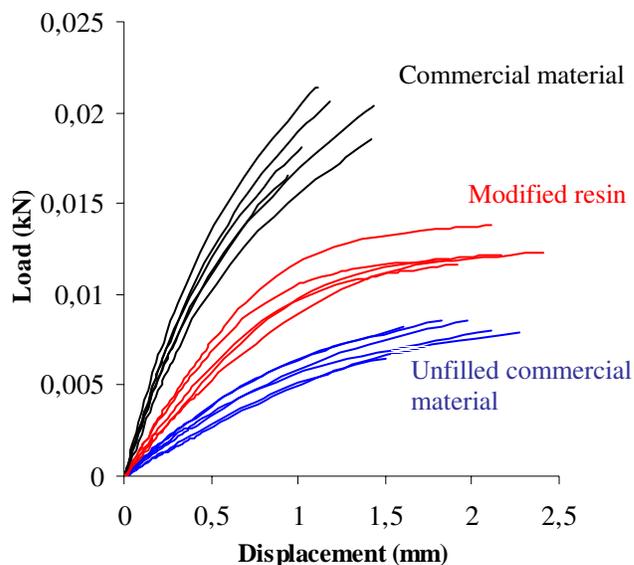


Figure 3: Observed load-displacement behavior of commercial material, unfilled commercial material and modified resin.

Results of the Figure 3 were reflected in the data of the Table 1. It was found that flexural modulus and flexural stress of the modified resin are higher than flexural properties of unfilled commercial material.

	Stress at max (MPa)	Young Modulus (MPa)
Commercial material	51.0	1970.6
Unfilled commercial material	22.8	541.6
Modified resin	28.0	756.0

Table 1: Average results for commercial material, unfilled commercial material and modified resin: flexural stress and flexural modulus.

3.5 SEM photomicrographs

Figure 4 shows the SEM image of the surface of two specimens. Figure 4 B shows that distribution of polymer nanoparticles is homogenous in the resin of the dental material.

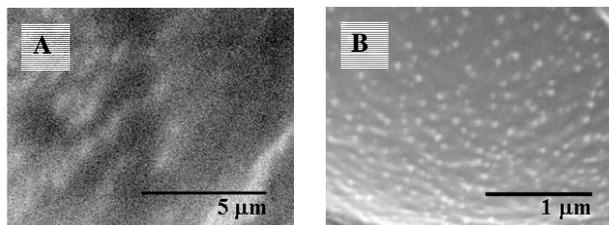


Figure 4: SEM micrographs of fracture surfaces of resin of commercial dental material (A) and of resin modified with RPNPs (B).

3.6 Analysis of volume shrinkage

It was found that volume shrinkage of modified resins in the all cases was lower than the contraction of unfilled commercial material. The polymerization shrinkage increased with the concentration of pendant vinyl groups in reactive polymer nanoparticles.

	Pendant conc. in polymer (%)	Volume shrinkage (%)
Commercial material	—	5.16
Unfilled commercial material	—	8.14
Modified resin 1	23.3	4.04
Modified resin 2	26.0	4.05
Modified resin 4	60.1	4.84

Table 2: Changes of volume shrinkage with concentration of pendant vinyl groups of polymers.

4 CONCLUSION

Reactive polymeric nanoparticles were prepared by free radical non-linear copolymerization in toluene from ST and EGDm. Size of nanoparticles was analyzed by SEM and the ratio of pendant vinyl groups was measured by NMR. SEM photographs of copolymer particles show that their size ranges from around 50 nm to 1.5 µm.

Resin of dental material was modified by reactive polymeric nanoparticles. Homogeneity, mechanical properties and volume shrinkage of modified resins was analyzed. Both flexural modulus and flexural stress of the modified resin are higher than flexural properties of unfilled commercial material. The polymerization shrinkage of modified resin was less than that of unfilled commercial material.

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