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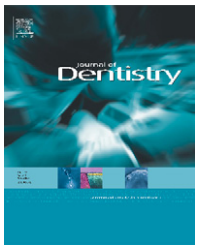

Synthesis and characterization of triethylene glycol dimethacrylate nanocapsules used in a self-healing bonding resin

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ARTICLE INFO

Article history:
Received 17 May 2011
Received in revised form
1 September 2011
Accepted 5 September 2011

Keywords:
TEGDMA
Nanocapsules
Dental adhesive
Self-healing

ABSTRACT

Objectives: To date, the production of highly durable dentine bonding is still a challenge. Self-healing bonding resins may provide a new direction for the improvement of the bonding durability. The objective of the current study was to synthesize polyurethane nanocapsules encapsulated with the core material triethylene glycol dimethacrylate (TEGDMA) for use as a major component in a self-healing bonding resin.

Methods: TEGDMA nanocapsules were synthesized via interfacial polycondensation in a miniemulsion, and the TEGDMA nanocapsules were then characterized via Fourier-transform infrared (FTIR) spectrometer, field emission scanning electron microscopy (FESEM), and high-performance liquid chromatography (HPLC) to investigate the morphology, the average TEGDMA loading (*DL*%), and encapsulation efficiency (*EE*%). The mechanical property of dental adhesive with different concentrations (0, 3, 6, 9, and 12 wt%) of the TEGDMA nanocapsules were also measured, and the cytotoxicity was investigated using an MTT assay.

Results: FTIR confirmed that the TEGDMA nanocapsules were successfully synthesized. These nanocapsules showed a high drug load. The bond strength of the dental adhesive incorporated with 9 wt% TEGDMA nanocapsules was significantly higher compared with those of the other groups ($P < 0.001$). Moreover, the biocompatibility of the dental adhesive was not affected by the incorporation of the TEGDMA nanocapsules.

Conclusions: The current study demonstrated the successful synthesis of TEGDMA nanocapsules, and the overall properties of the dental adhesive were not compromised.

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Abbreviations: TEGDMA, triethylene glycol dimethacrylate; IPDI, isophorone diisocyanate; MTT, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide; DMEM, Dulbecco's modified Eagle's medium; FBS, foetal bovine serum; SDS, sodium dodecyl sulphate; FESEM, field emission scanning electron microscopy; HPLC, high performance liquid chromatography; FTIR, Fourier transform infrared ray; μTBS, micro-tensile bond strength; DW%, drug loading; *EE*%, encapsulation efficiency.

0300-5712/$ – see front matter
doi:10.1016/j.jdent.2011.09.001

1. Introduction

The immediate bonding effectiveness of contemporary dentine adhesives has become favourable with the development in adhesive dentistry. However, the limited durability of dentine adhesives in vivo is still a major shortcoming.[1] A number of factors affect the durability of adhesives in clinical applications, such as the degradation of exposed collagen fibrils, especially for etch and rinse adhesives, and the hydrolytic breakdown of adhesive monomers primarily for self-etch adhesives.[2] Microcracking induced by thermal and mechanical fatigue is also a long-standing problem that affects the durability of adhesives.[3] At present, methods of enhancing the durability primarily focus on the built-in dentine-associated matrix metalloproteinases (MMPs) inhibitors or the improvement of the bonding technique, such as ethanol wet-bonding.[4,5] However, there are little studies focused on enhancing the durability by healing the microcracks.

Tensile loading, fatigue loading, and thermal cycling can result in the formation of microcracks in dental adhesives. The nucleation of microcracks around weak links can propagate continuously, resulting in the degradation of mechanical properties, formation of pathways for the entry of liquids and bacteria, and complete material failure.[6,7] Studies have indicated that the weak links in dental bonding adhesion are located in the hybrid layer, the quality of which is important to bond strength.[8,9] Therefore, to improve the durability of dental adhesives, microcracks should be repaired before the integrity of the adhesive is destroyed.

Scientists have recently proposed self-repair ideas that may increase the life expectancy of composite materials.[10–12] The discovery of a self-healing resin based on the use of microcapsules is a research breakthrough. White et al.[13] successfully synthesized a self-healing epoxy resin composite through the encapsulation of a healing agent within the microcapsules. These encapsulations were embedded with a catalyst capable of polymerizing the healing agent in a polymer matrix. The rationale for the self-healing design is that when cracks form in the matrix, they rupture the microcapsules, releasing the healing agent into the crack plane through capillary action. The healing agent then comes into contact with the catalyst, triggering polymerization, and finally bonds until the crack faces close.

To date, the use of a self-repair bonding resin to improve the durability of dental adhesives is an open and intriguing approach. Meanwhile, the rapid development in nanoscale controlled drug delivery technology[14,15] provides the possibility of a 'smart' material for the purposes of self-healing in the oral environment.

Scientists have postulated that a chemical repair monomer encapsulated in a polymer can be an important factor in developing self-repair materials.[12] Polyurethanes, an important class of polymers, are widely used in the medical field to encapsulate a wide range of active agents.[16] The excellent physicomechanical properties, high flexibility, and relatively good biocompatibility of polyurethanes make them suitable shell materials for encapsulation and meet the requirements of self-healing nanocapsules.[17,18] Moreover, triethylene glycol dimethacrylate (TEGDMA) is a frequently used monomer with low viscosity, making it a suitable candidate as a core material.[19] Therefore, a hypothesis on the synthesis of nanocapsules encapsulated with an active monomer that exhibits the self-healing function of dental adhesives based on the aforementioned rationale is proposed.[13]

The primary objective of this pilot study was to investigate the synthesis and characterization of polyurethane nanocapsules containing TEGDMA via interfacial polycondensation in a miniemulsion for use as a major component in self-healing bonding resins. The mechanical properties and cytotoxicity were also determined to investigate the compatibility of TEGDMA nanocapsules with a commercial dental adhesive.

2. Materials and methods

2.1. Materials

Isophorone diisocyanate (IPDI) and TEGDMA were obtained from Aldrich Chemical Company, Inc., USA. 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was purchased from Sigma Chemical Company. Dulbecco's modified Eagle's medium (DMEM) and foetal bovine serum (FBS) were from Gibco Company. All other reagents were of analytical grade.

2.2. Fabrication of the TEGDMA nanocapsules

The TEGDMA nanocapsules were encapsulated in polyurethane by interfacial polycondensation in miniemulsion of IPDI and 1,6-hexanediol as reported by Torini et al.[20] Detailed process could be seen in our precious work[21] and the brief procedure was showed in Fig. 1.

2.3. Morphological analysis

The TEGDMA nanocapsules were dispersed in distilled water as mentioned above and then one droplet was dropped on tin foil. The sample was dried at room temperature and observed under FESEM (Sirion 200, FEI, Netherlands) at 15 kV.

2.4. TEGDMA loading and encapsulation efficiency

Nanocapsules loaded with TEGDMA (10 mg) were dissolved in isopropanol followed by 30 min on ultrasounds. After extraction, it was diluted to volume with distilled water to 10 ml. Then 1 ml solution was extract and diluted to volume with mobile phase to 10 ml. The resulting solution was filtered through 0.45 μm PTFE membrane filters. And then the filtered solution (20 μl) was injected into a high performance liquid chromatographic (HPLC) apparatus. And the amount of TEGDMA entrapped was determined by HPLC.[22,23] A ChromoQuest thermoquest France SA instrument was used with Agilent HC C-18 (5 μm, 250 mm × 4.6 mm). The mobile phase consisted of methyl cyanides and water (55:45). The flow rate was 1 ml/min. A volume of 20 μl loop was injected at temperature of 25 °C. TEGDMA was detected using UV spectrophotometer (Secomam, Anthelie, France) at the λ_{max}