



## Biphenyl liquid crystalline epoxy resin as a low-shrinkage resin-based dental restorative nanocomposite

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### ARTICLE INFO

#### Article history:

Received 12 February 2012

Received in revised form 5 July 2012

Accepted 20 July 2012

Available online 27 July 2012

#### Keywords:

Liquid crystalline

Dental restorative material

Nanocomposite

Post-gelation shrinkage

Cytotoxicity

### ABSTRACT

Low-shrinkage resin-based photocurable liquid crystalline epoxy nanocomposite has been investigated with regard to its application as a dental restoration material. The nanocomposite consists of an organic matrix and an inorganic reinforcing filler. The organic matrix is made of liquid crystalline biphenyl epoxy resin (BP), an epoxy resin consisting of cyclohexylmethyl-3,4-epoxycyclohexanecarboxylate (ECH), the photoinitiator 4-octylphenyl phenyliodonium hexafluoroantimonate and the photosensitizer champhorquinone. The inorganic filler is silica nanoparticles (~70–100 nm). The nanoparticles were modified by an epoxy silane of  $\gamma$ -glycidoxypolytrimethoxysilane to be compatible with the organic matrix and to chemically bond with the organic matrix after photo curing. By incorporating the BP liquid crystalline (LC) epoxy resin into conventional ECH epoxy resin, the nanocomposite has improved hardness, flexural modulus, water absorption and coefficient of thermal expansion. Although the incorporation of silica filler may dilute the reinforcing effect of crystalline BP, a high silica filler content (~42 vol.%) was found to increase the physical and chemical properties of the nanocomposite due to the formation of unique microstructures. The microstructure of nanoparticle embedded layers was observed in the nanocomposite using scanning and transmission electron microscopy. This unique microstructure indicates that the crystalline BP and nanoparticles support each other and result in outstanding mechanical properties. The crystalline BP in the LC epoxy resin-based nanocomposite was partially melted during exothermic photopolymerization, and the resin expanded via an order-to-disorder transition. Thus, the post-gelation shrinkage of the LC epoxy resin-based nanocomposite is greatly reduced, ~50.6% less than in commercialized methacrylate resin-based composites. This LC epoxy nanocomposite demonstrates good physical and chemical properties and good biocompatibility, comparable to commercialized composites. The results indicate that this novel LC nanocomposite is worthy of development and has potential for further applications in clinical dentistry.

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### 1. Introduction

Methacrylate resin-based dental restorative materials exhibit intrinsic shrinkage problems resulting from the free volume reduction that occurs due to the linking of methacrylate monomer and oligomer during photocuring. This free volume reduction is at the nanometer scale (i.e. reduced entropy) and cannot be compensated for by very small picometer-scale volume increases, such as those that occur when carbon–carbon sigma bonds (154 pm) are formed

from carbon–carbon double bonds (147 pm) during polymerization. The contraction stress of shrinkage can lead to tooth structure damage and the formation of internal gaps between restorative materials and the original tooth structure [1–3]. Polymerization shrinkage can be reduced using large molecule resins or other resin types [4]. Special methacrylate monomers and oligomers have been designed to reduce the polymerization shrinkage of restorative resins [5–9]. Recently, liquid crystalline (LC) and crystalline acrylates have been reported to reduce shrinkage. Photopolymerization of methacrylate resins via visible light irradiation is an exothermic reaction. The released heat melts the crystalline acrylate and results in a disordered structure (order-to-disorder transition). The volume expansion from this type of order-to-disorder

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