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A physico-chemical explanation of the post-polymerization shrinkage in dental resins

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Summary The main problem of a methacrylated dental resin's photopolymerization is the shrinkage phenomenon. This occurs, as expected, during light irradiation but also, unexpectedly, during about 24 h after photopolymerization (i.e. during the so-called 'post-polymerization' stage). During this period, the conversion degree does not change significantly (no more initiation, very limited, if any, propagation reaction) but free radicals concentration decreases.

Objectives: To better understand what happens during the 24 h after the photopolymerization, a thermal study of these resins is investigated at first and an explanation is then discussed.

Methods: In this paper, the glass transition temperatures (T_g) are measured at 0 and 24 h by DMA. The post-shrinkage phenomenon is observed by TMA. Conversion degree (DC) is followed by Raman and free radical decay by ESR spectroscopy.

Results: T_g increases significantly during post-polymerization (55–80 °C). The same samples were studied by TMA at room temperature and shrinkage is observed. The fact that the degree of conversion (DC) does not increase significantly and that the 'post-shrinkage' occurs at $T < T_g$ leads to the hypothesis that a physical phenomenon should occur which can, in turn, be responsible for a secondary chemical phenomenon (post-polymerization).

Significance: The proposed explanation is that, as photopolymerization of dental resins is very fast, a large excess of free volume is trapped in non-equilibrated samples. As they have no time to return to an equilibrium state, free volume should decrease below T_g and samples do physically shrink during the first 24 h. As a consequence, free radicals can come into 'contact' and undergo limited propagation

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but significant termination justifying the decrease in overall radical concentration.

Introduction

Nowadays dental resins are widely used by dentists because they are at first very esthetic in comparison with amalgam and there is no mercury release. However, shrinkage occurs during tooth restoration, which is the main problem for dentists. A clinical solution has been proposed which is to fill cavities layer-by-layer [1, 2] with dental resins in order to reduce shrinkage and to reach greater depths of cure [3]. But this incrementalization technique is tedious to perform adequately, can cause contamination and should not reduce shrinkage effects [4,5]. Therefore, different layer-by-layer filling techniques [6] to restore cavities are proposed to reduce it and changes in the organic matrix are also proposed by adding or by replacing some molecules [7]. Many theoretical studies have been done on this subject to understand and to reduce shrinkage. Different measurement techniques were used to follow and to understand this phenomenon. Mercury [8,9], water [10] and gas [11] dilatometric techniques have been investigated. Shrinkage can be also measured by the change of buoyancy of a material in water [12], by a linear displacement transducer [13,14] or by the strain gage method [15] and by laser interferometry [16]. These studies concluded that an important shrinkage appears during the visible light illumination of the organic matrix due to radical polymerization. This shrinkage has been extensively studied and is assigned to a volume decrease due to the substitution of van der Waal's links by (shorter) covalent bonds [17]. Another, but smaller shrinkage was also shown to occur after polymerization during about 24 h.

In the literature, this latter shrinkage is, generally, assigned to a 'post-polymerization' phenomenon [18]. However, sufficient molecular mobility is required for any chemical phenomenon occurring in the matrix [19]. On one hand, a gel effect [20] occurs during radical polymerization, increasing the concentration of free radicals which cannot terminate due to their reduced mobility in the matrix. On the other hand, a vitrification of the matrix occurs and free radicals [21] and remaining double bonds [22] are 'quenched' in the organic matrix. Therefore, during the phenomenon called 'post-polymerization' or 'post-shrinkage' by authors, it is very unlikely that free radicals have enough mobility to induce any observable polymerization. This phenomenon should thus not be assigned to a simple chemical process. It is the aim of this paper to explain which phenomenon occurring in the solid state can be responsible for this post-polymerization effect.

In this article, all the phenomena which occur in the organic matrix just after photopolymerization, were studied. At first, in order to determine the glass transition temperature of the organic matrix, a careful thermal study was performed using a Dynamical Mechanical Analyzer (DMA). Thermal Mechanical Analysis (TMA) was also performed to study the 'post-shrinkage' phenomenon at precise temperatures. Then, using TMA and density column results, a model is proposed which could explain the origin of this post-shrinkage, and is supported by measurements of Young modulus, by Raman and ESR spectroscopy.

Materials and methods

The methacrylated resin studied was composed of Bisphenol A Glycidyl diMethAcrylate (Bis-GMA) (Heraeus Kulzer, Dormagen, Germany), TriEthylene Glycol diMethAcrylate (TEGDMA) (Aldrich) (7:3), and of an initiator system (1% in weight of camphorquinone and tertiary amine from Aldrich), and it was light cured. This organic matrix represented nearly 20% by weight of the dental resin, the other part was composed of inorganic fillers. This study was, however, focused on the organic matrix alone.

Samples were photopolymerized with a visible light device 'Translux Energy' (Heraeus Kulzer, Dormagen, Germany) for 40 s with an intensity of 900 mW/cm^2 under 'the conventional mode.'

Dynamical mechanical analyzer (DMA)

This technique allows T_g values of the organic matrix to be measured. The DMA (DMA/SDTA861e from Mettler-Toledo) technique yields a complex mechanical modulus from which T_g values can be deduced. The organic matrix is placed in a home-made mold of 1 mm thick and 10 mm of diameter where it is photocured. Two identical disks are molded and placed symmetrically