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Influence of curing protocol on selected properties of light-curing polymers: Degree of conversion, volume contraction, elastic modulus, and glass transition temperature

Magali Dewaele[a,b,*], *Erik Asmussen*[c], *Anne Peutzfeldt*[c], *E. Christian Munksgaard*[c], *Ana R. Benetti*[d], *Gauthier Finné*[a], *Gaëtane Leloup*[e], *Jacques Devaux*[a]

[a] *Laboratory of Chemistry and Physics of High Polymers, Université catholique de Louvain, Louvain-la-Neuve, Belgium*
[b] *Department of Prosthodontics, School of Dentistry and Stomatology, Université catholique de Louvain, Brussels, Belgium*
[c] *Department of Dental Materials, School of Dentistry, University of Copenhagen, Copenhagen, Denmark*
[d] *Department of Operative Dentistry, Endodontics and Dental Materials, Bauru School of Dentistry, University of São Paulo, Bauru SP, Brazil*
[e] *Department of Operative Dentistry, School of Dentistry and Stomatology, Université catholique de Louvain, Brussels, Belgium*

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ABSTRACT

Objectives. The purpose of this study was to investigate the effect of light-curing protocol on degree of conversion (DC), volume contraction (*C*), elastic modulus (*E*), and glass transition temperature (T_g) as measured on a model polymer. It was a further aim to correlate the measured values with each other.

Methods. Different light-curing protocols were used in order to investigate the influence of energy density (ED), power density (PD), and mode of cure on the properties. The modes of cure were continuous, pulse-delay, and stepped irradiation. DC was measured by Raman micro-spectroscopy. *C* was determined by pycnometry and a density column. *E* was measured by a dynamic mechanical analyzer (DMA), and T_g was measured by differential scanning calorimetry (DSC). Data were submitted to two- and three-way ANOVA, and linear regression analyses.

Results. ED, PD, and mode of cure influenced DC, *C*, *E*, and T_g of the polymer. A significant positive correlation was found between ED and DC ($r = 0.58$), ED and *E* ($r = 0.51$), and ED and T_g ($r = 0.44$). Taken together, ED and PD were significantly related to DC and *E*. The regression coefficient was positive for ED and negative for PD. Significant positive correlations were detected between DC and *C* ($r = 0.54$), DC and *E* ($r = 0.61$), and DC and T_g ($r = 0.53$). Comparisons between continuous and pulse-delay modes of cure showed significant influence of mode of cure: pulse-delay curing resulted in decreased DC, decreased *C*, and decreased T_g. Influence of mode of cure, when comparing continuous and step modes of cure, was more ambiguous.

* *Corresponding author at*: Cliniques universitaires St-Luc, Ecole de médecine dentaire et de stomatologie, avenue Hippocrate 10/bte5732, 1200 Bruxelles, Belgium. Fax: +32 2 764 90 62.
E-mail address: Magali.Dewaele@uclouvain.be (M. Dewaele).

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A complex relationship exists between curing protocol, microstructure of the resin and the investigated properties. The overall performance of a composite is thus indirectly affected by the curing protocol adopted, and the desired reduction of C may be in fact a consequence of the decrease in DC.

1. Introduction

It is widely admitted that the influence of photopolymerization on the final properties of resin composites is of major importance. Literature [1–5] has shown that the properties of a light-curing resin composite are mainly influenced by the amount of energy delivered during irradiation. The total amount of energy per unit area, the so-called energy density (ED) is the product of the power per unit area (power density: PD) by the duration of irradiation (curing time). For a given ED, different combinations of PD and curing time may be used to cure the composite materials.

Contradictory data have been published about the effect of variation in the combination of PD and exposure duration. Contrary to the "total energy concept" (referring to the reciprocity between power density and exposure duration), recent studies have demonstrated that for each ED, the combination of PD and exposure duration had a significant influence on degree of conversion, on extent of crosslinking and on physical properties [3].

The light from dental photocuring devices can be delivered in different modes: continuous, pulse-delay or stepped irradiation. The continuous mode delivers the same PD uninterruptedly throughout the entire exposure period. The pulse-delay mode initiates cure by a short flash of light followed by a delay of one or more minutes before the final polymerization is performed. In the step-cure mode, a low PD is used during the first part of the polymerization period and a higher PD is used towards the end of the irradiation. The pulse-delay and the stepped mode of cure are so-called "soft-start" modes of cure.

The soft-start modes of cure were introduced with the purpose of slowing down the polymerization reaction, which is inevitably accompanied by contraction of the material [6]. Soft-start curing modes result in significantly reduced gap formation in cavity margins because of contraction stress relief by flow [7–14]. However, few studies have evaluated the effect of curing mode on the volume contraction itself. Some authors found soft-start curing to combine increased marginal integrity with identical [15] or superior physical properties when compared to continuous curing [11]. Adversely, soft-start techniques have resulted in either decreased degree of conversion (DC) as compared to the one of the continuous mode, or similar DC but at the same time in polymers of lower crosslink density, and thus of decreased mechanical properties [16–19].

As hypothesized in a previous study [17], it is conceivable, that the different light-curing modes will lead to polymers of different network structure, even though the DC is the same. The DC does not give a complete characterization of polymer structures because polymers of similar DC may have different extent of crosslinking [16–18]. This may occur as a result of the soft-start modes of cure (pulse or step-cure mode) probably due to the formation of relatively fewer growth centers, which may result in a more linear polymer, with decreased crosslinking. The increased concentration of crosslinks has been associated with increased physical properties and stability of polymers [16,20].

It has been shown [20,21] that the extent of crosslinking of a polymer may be assessed by measurements of the glass transition temperature (T_g). T_g is an important parameter for polymer characterization as it marks a region of dramatic changes in the physical properties of the polymer. The T_g-value represents the temperature region at which the polymer is transformed from a glassy material into a rubberlike one. Crosslinking reduces molecular mobility and thus gives rise to increased apparent T_g [22]. The curing procedure may influence the regularity of the network and the crosslink density, and this may be reflected in the T_g.

To improve the overall performance of light-cured dental polymers, a detailed understanding of the effects of mode of irradiation on properties and how these properties are related to each other is necessary. The present study represents an effort in this direction. It was the aim of the study to determine, on the same experimental dental polymer, degree of conversion, volume contraction, elastic modulus, and glass transition temperature in relation with the curing protocol. The working hypothesis was that the total energy density and, for each level of ED, that the power density and the mode of cure, have an effect on the selected properties. A further aim was to attempt to correlate the data obtained for these properties with each other. In a further study [23] the data are correlated with softening and elution of monomers in ethanol as measured on identical polymers subjected to the same curing protocols.

2. Materials and methods

The experimental resin used in this study was composed of Bis-GMA (bisphenol-A-glycidyl dimethacrylate, Heraeus Kulzer, Germany) and TEGDMA (95% triethyleneglycol dimethacrylate, Aldrich, Belgium) at a molar ratio of 1:1, along with 0.5 wt% CQ (97% camphorquinone, Aldrich) as visible light initiator and 0.5 wt% DABE (97% N,N-dimethyl-*p*-aminobenzoic acid ethylester, Aldrich) as co-initiator.

Cylindrical specimens were fabricated in a brass mold. The specimens were covered on both sides with a transparent film (Mylar) and irradiated from one side only. Specimens used for degree of conversion and contraction measurements (height: 2 mm, diameter: 5 mm) and specimens used for elastic modulus and glass transition temperature measurements (height: 1 mm, diameter: 3 mm) were of different size as dictated by the dimension requirement of the measuring device.