

***In situ* Characterization of Conversion and Polymerization Shrinkage Simultaneously in Photo-cured Hybrid Systems**

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Introduction

It is well-known that, polymers exhibit the inherent problem of volumetric shrinkage when cured, because of the formation of short-range covalent bonds as well as the reduced mobility between the monomer units [1]. Polymerization shrinkage creates internal stresses which may lead to surface and structural flaws. As a result, polymerization shrinkage is of great importance in studies of polymerization kinetics [1], coatings [2], manufacturing of aspheric lenses [3], stereolithography [4], and photocuring of dental restorative resins [5-8]. On the other hand, the degree of polymerization or conversion plays a significant role in determining the ultimate physical and mechanical properties of the material. Incomplete polymerization also predisposes the material to degradation and leaching. Therefore, both parameters, high conversion and low shrinkage, are indispensable for getting optimal material properties. However, except for expanding monomer systems, an optimal degree of conversion and minimal polymerization shrinkage are generally antagonistic goals, as the higher the conversion in a material, the greater its shrinkage. This trade-off between degree of conversion and polymerization shrinkage is an important factor in the development and selection of polymer based material for practical applications.

With respect to hybrid systems, the challenge for exploring materials with both high degree of conversion and reduced shrinkage seems to be rather straightforward and flexible: to favorably affect conversion, polymerization shrinkage as well as stress development based on the choice of proper comonomer composition and polymerization sequence. The present study represents a preliminary effort in this direction by evaluating polymerization shrinkage development within the selected hybrid systems. In semi- and full-IPN systems, structural features associated with the different photopolymerization profiles could potentially be locked into the final polymer morphology and be used to controllably alter polymer properties.

The objective of this study was to determine whether a sequential photopolymerization process produces less polymerization shrinkage but adequate final conversion in methacrylate/vinyl ether hybrid system than in either a typical simultaneous polymerization process of the same hybrid system or the corresponding homopolymerization processes. The potentially unique relationship between degree of conversion and volumetric shrinkage during the hybrid polymerization reactions will be evaluated.

Experimental

Materials

The following compounds were used in this study:

- vinyl ether monomer: tri(ethylene glycol) divinyl ether (TEGDVE); methacrylate monomer: tri(ethylene glycol) dimethacrylate (TEGDMA) (all from Aldrich).
- In this study, we have used (4-((2-hydroxytetradecyl)oxy)phenyl)phenyl iodonium hexafluoroantimonate (ISbF₆) as cationic type initiator and 2,2-dimethoxy-phenylacetophenone (DMPA) as free radical type initiator (all from Aldrich).

Equipment

The polymerization reaction kinetics was followed *in situ* by FT-near-infrared (NIR) spectroscopy (Nicolet Nexus 670) equipped with an extended KBr beam-splitter and an MCT/A detector. To initiate photopolymerization, a UV-light source (Novacure, EXFO, Mississauga, Ontario, Canada) filtered to 320-390 nm was directed to the sample through a liquid light guide, with the irradiation intensity at the sample of 4 mW/cm² as measured with a radiometer (IL1400A, International Light, Inc., Newburyport, MA, USA). All photopolymerizations were conducted at room temperature.

Linear shrinkage was measured with an ACTA linometer (Academisch Centrum Tandheerkunde Amsterdam, 1066 EA Amsterdam, The Netherlands). Disc-shaped samples with approximately 7 mm diameter, which were pure monomers or equimolar mixtures of methacrylate and vinyl ether with the various photoinitiator combinations, were placed on the linometer's sample carrier, an aluminum disk. A glass slide was laid on the sample, thereby compressing the sample to a thickness of 1 mm. During each measurement run, the shrinkage forces exerted by the polymerizing system were able to pull the aluminum disk upwards. Based on the displacement values, the linear polymerization shrinkage was calculated then converted to volumetric shrinkage by the integrated software. The volumetric shrinkage/time curve of the hybrid system was recorded continuously for a period of 30-120 mins at room temperature. At least three measurements per system were conducted.

Characterization technique

The kinetics of the hybrid methacrylate/vinyl ether polymerizations was monitored by FT-NIR spectroscopy. The absorbance peak area method was used to calculate conversion. The two =CH₂ first overtone absorption bands at 6164 cm⁻¹ and 6192 cm⁻¹ in the NIR region were used to follow the concentration of methacrylate and vinyl ether double bonds, respectively. A second-derivative deconvolution method allows the calculation of conversion for the individual monomers during the polymerization separately [9]. During the photopolymerization, data were collected at a rate of about one spectrum per second. Data processing was performed with Nicolet's OMNIC (Nicolet) software.

Results and Discussion

In this study, a modified linometer coupled with NIR for the purpose of directly monitoring continuous volumetric polymerization shrinkage evolution as a function of conversion was constructed and evaluated. This coupled technique affords practically unprecedented simple operation procedure and experimental set-up, combining the advantages both linometer and NIR could possibly offer.

This coupled approach was applied to selected hybrid systems, where combinations of methacrylate and vinyl ether monomers were photopolymerized with the onset and cure kinetics of the individual monomers controlled through concentrations of free radical and cationic photoinitiators. The possibility of achieving both maximized degree of conversion and reduced shrinkage for the selected hybrid systems was investigated.

Table 2 shows a comparison of the effects of two initiator combinations on the

volumetric shrinkage and conversion of TEGDMA/TEGDVE hybrid polymerizations, respectively. All the hybrid samples were irradiated with 4 mW/cm² light intensity for 30 mins. For system I (0.2 wt% DMPA + 0.2 wt% ISbF₆), an expansion was noticed around 1150 s, followed by a slow and slight increase in sample volume reaching a final shrinkage of 13.9 % at 7200 s. With respect to system II, increasing the DMPA concentration from 0.2 % to 0.5 % and decreasing the iodonium salt concentration from 0.2 % to 0.1 % by weight, a more dramatic expansion was observed starting from 260 s, followed by a continuous decrease in shrinkage value. The final shrinkage of 6.6 % at 7200 s is substantially lower than that of system I or the corresponding homopolymerizations (Table 1). This reveals that the use of the TEGDVE monomer as a latent reactive diluent or plasticizer [9] leads to reduced polymerization rate of TEGDMA and allows more time for molecular rearrangements, drastically decreasing the final polymerization shrinkage of system II.

Table 1. Final polymerization volumetric shrinkage and conversion data for TEGDMA and TEGDVE homopolymerization systems at room temperature.

Monomer	TEGDMA	TEGDMA	TEGDVE
Initiator (wt%)	DMPA (0.2)	DMPA (0.5)	ISbF ₆ (0.2)
VS (%)	12.8±0.5	11.6	20.2 ± 0.3
Theoretical VS (%) [1]	11.9	12.4	22.0
Conversion (%)	70.5 ± 0.1	73.8 ± 0.2	100

Table 2. Final polymerization volumetric shrinkage and conversion data for TEGDMA/TEGDVE hybrid systems at room temperature.

TEGDMA+TEGDVE (DMPA / ISbF ₆) (wt%)	0.2 / 0.2 (I) (@ 7200 s)	0.5 / 0.1 (II) (@ 7200 s)
VS (%)	13.6 ± 0.3	6.4 ± 0.3
Theoretical VS (%)	15.8	15.0
Time to reach max. VS	~ 1150s	~ 260s
Conversion (%) (TEGDMA/TEGDVE)	(67 ± 2) / (96 ± 1.5)	(91.5 ± 2) / (63 ± 1.2)

The shrinkage control is closely related to the morphological changes during curing [10-12]. Merle et al. have reported that the shrinkage compensation mechanism is governed by the morphology resulting from phase separation and thermally-induced or kinetically related excess free volume formation [13]. If both free radical and cationic initiations are active, there will be some tendency for methacrylate chains to terminate and convert to cations that can then initiate vinyl ether polymerization. This gives a covalent connection in the form of a block copolymer. If the cationic initiation is delayed with respect to the free radical, the methacrylate chains will be more likely to undergo normal biradical termination and then the subsequent vinyl ether polymerization will more likely be separate from the methacrylate network. These processes would favor enhanced phase separation of the sequentially polymerized hybrid systems.

Conclusions

Coupling dynamic shrinkage measurement with FT-NIR provides a highly informative technique to examine volumetric shrinkage evolution during polymerization. This approach is applied to selected methacrylate/vinyl ether hybrid systems, which provide significant potential

for reduction of polymerization shrinkage. Through controlled sequential photopolymerization, the methacrylate monomer can achieve high conversion with the vinyl ether initially acting as solvent, which subsequently also polymerizes to high extent. This work represents a preliminary effort towards novel low-shrinkage biomaterials.

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