LARS-ÅKE LINDÉN*), JULITA JAKUBIAK**)

Contraction (shrinkage) in polymerization

Part II. DENTAL RESIN COMPOSITES***)

Summary — A review with 78 references covering the linear and volumetric contraction producing internal stresses in photocured dental restorative resin composites. The stresses are partially reduced by the flow of resin, ingress of air bubbles, and absorption of water. Computer simulations allow to predict the directions of shrinkage vectors (Fig. 4). Polymerization shrinkage of (meth)acrylate monomers can be reduced by fillers (up to 80%, Table 4) or prepolymers added to the base monomer mix. Free-radical ring-opening polymerization of suitable monomers decreases volume contraction because some covalent bonds are cleft to give near Van der Waals bond distances.

Key words: polymerization contraction, linear and volumetric shrinkage, dental composites, stress formation, stress control.

The primary problem in photocuring of dental resin composites is the polymerization contraction (linear, S_L, and/or volume shrinkage, S_V) [1]. This entails numerous undesirable results such as internal stresses, micro-cracks, and debonding at the filler particle/resin interface, resulting in accelerated degradation through reduced mechanical strength and diminished abrasion resistance. The external loss of adhesion produces marginal gaps at the composite/tooth interface and ultimately results in secondary caries and staining.

FORMATION OF SHRINKAGE IN DENTAL RESIN COMPOSITES

The rate of shrinkage formation in dental resin composites is fastest during the first few minutes of polymerization and then a plateau is reached (Fig. 1) [2]. Residual polymerization continues to occur for at least the following 24 hours and can result in additional shrinkage [3]. Shrinkage as low as 2% by volume can give rise to stress that may result in failure of the composite to adhere to dentine [4].

The shrinkage of dental resin composites is basically affected by:

— Light intensity and the irradiation process [5—8].

A linear relationship occurs between light intensity and amount of shrinkage [6]. The rate of shrinkage formation in a photocured composite is fastest during the first 30—40 seconds of the polymerization reaction [9]. Higher light intensities may cause more rapid development of polymerization contraction forces. However, doubling the light intensity increases the depth of curing by approximately 15% only [10, 11].

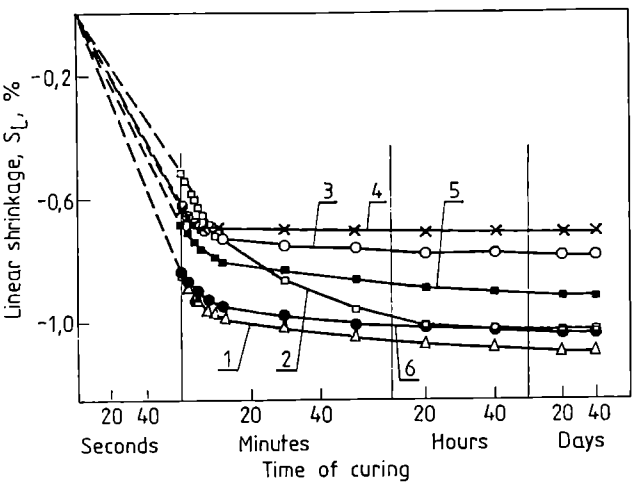


Fig. 1. Linear shrinkage (S_L) as a function of time of curing for some commercial dental restorative materials: 1 — Heliomolar, 2 — Heliomolar, 3 — Helioprogress, 4 — Silux, 5 — Prisma APH, 6 — Coltene (cf. Table 4) [2]

— Structures and compositions of different monomers in the resin composite [5, 12—16].

— Properties of the composite material itself [2, 17—19].

— Filler content [20].

*) Polymer Research Group, Department of Dental Biomaterial Science, Karolinska Institute, Box 4064, S-141 04 Huddinge (Stockholm), Sweden and Department of Chemistry and Chemical Engineering Technical and Agricultural Chemistry, Seminaryjna 3, 85-326 Bydgoszcz, Poland.

**) Department of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Cracow, Poland.

***) Part I — "Polimery" 2001, 46, No 7—8.

— Degree of monomer conversion

The degree of conversion can be maximized by including a high percentage (40—50%) of tri(ethylene glycol) dimethacrylate (TEGDMA) in the formula of the resins [21, 22].

— Degree of cross-linking of polymers [15]

A higher degree of cross-linking can give rise to a higher amount of shrinkage.

— Post-gel curing

The total amount of shrinkage is commonly four times as high as the amount of post-gel shrinkage [21—24].

— Geometry effects and the "configuration factor" (the ratio of bound to unbound surface) [5, 17, 25—27].

— Compatibility of the substrate materials [17, 28, 29].

With incompatible substrate materials a considerable curing stress, likely to be destructive, will develop in thin bonded resin layers. However, as the curing contraction of such thin layers is small in the absolute sense, a small amount of strain of the substrates should suffice to cause a substantial degree of stress relief. The influence of compatibility of the set-up is most pronounced in layers around 100 μm thick [29].

Shrinkage reduces the size of the final product, *i.e.*, its thickness and volume. Stresses can lead to defects, *e.g.*, buckling, cracking, curling, warping, void formation, delamination, and poor adhesion (Fig. 2), that degrade

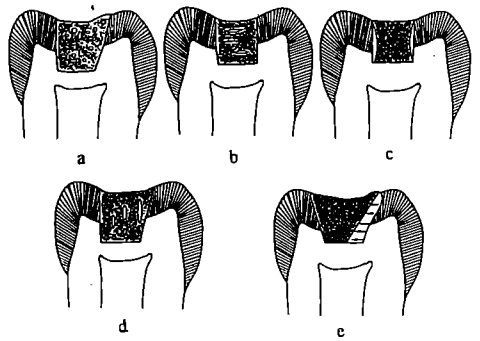


Fig. 2. Shrinkage problems with restorative resin composites: (a) void formation, (b) stress cracking, (c) poor adhesion, (d) delamination and (e) composite warping

the final physical and mechanical properties of the cured composite.

The direction of shrinkage can be represented by shrinkage vectors [24]. It is affected by various factors:

— shape of the restorative cavity in the tooth;

— rate and degree of polymeric conversion in different locations in the restoration;

— boundary conditions which include bonding to the cavity walls and flow at the free surface of restoration.

While composites are being photocured, the amount of shrinkage can vary from place to place, depending on (local) light intensity, position of the light source (Fig. 3), curing depth [8], and reaction rate [30,31]. The position of the light source can affect shrinkage vectors, provided the light intensity is low enough to create a gradient in the polymerization velocity within the bulk of the resin. Lower intensities usually slow down the rate of conversion [10, 32—34], and result in lower post-gel shrinkage amounts [23, 34, 35]. Since the intensity of the curing light is the highest at the surface and decreases as the light penetrates deeper into the composite, the superficial layers will shrink more and faster than deeper layers. In the photo-curing of composities, shrinkage is directed towards the surface [36] but it is not affected by the orientation of the incoming light beam [10, 24].

Comparison of shrinkage amounts established in commercial resin compositions is inconclusive because the chemical compositions of monomers (or polymer) and the filler content of the material tested are not identical even if produced by the same manufacturer. These factors are particularly critical when samples are small (10—50 mg).

STRESS DEVELOPMENT BY SHRINKAGE

The photopolymerization shrinkage of a dental resin composite restoration can create contraction forces that may disrupt the bond to the cavity walls [18, 25—27, 37]. This competition between the mechanical stress in polymerizing resin composites and the bond of adhesive resins to the walls of restorations is one of the main causes of marginal failure and subsequent micro-leakage observed in resin restorations [38]. The gap formed can be fairly significant and allow the oral and pulpal fluids and bacteria to invade [26, 39, 40]. Bacterial toxins that invade and grow in the space (gap) between the filling and the cavity wall are the main cause of pulpal irritation in the teeth restored with resin composites. Micro-leakage, leading to secondary caries, is the predominant reason for replacement of composite resin restorations. In order to avoid this problem, the resin composite should be bonded to the cavity walls. Bond strength must overcome contraction stresses to yield a stable marginal adaptation of a resin composite to the tooth cavity [38]. However, on preventing shrinkage, contractile forces are produced in the material, which place a strain on the restored tooth and endanger the coherence of the bonding [26, 38].

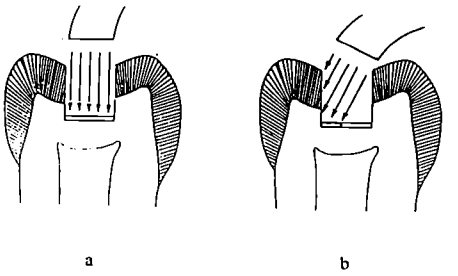


Fig. 3. Position of a light source above the polymerizing resin in tooth cavity during photocuring procedure: (a) correct, (b) incorrect

ROLE OF FLOW OF RESIN IN STRESS REDUCTION

The amount of stress generated in photopolymerization of dental resins is related to the extent of restriction of polymerization shrinkage [9, 18, 24—26, 37, 38, 41—46]. "Restricted shrinkage" occurs on bonded surfaces, "unrestricted shrinkage" occurs on free, unbonded surfaces. "Free shrinkage" occurs only in an experimental set-up, *e.g.*, in a dilatometer. Free-shrinkage data cannot be simply extrapolated to clinical situations, since effective shrinkage is the result of a complex set of parameters, which includes the shape, bonding, environment, and curing history. Depending on the material, the magnitude of "free shrinkage" varies from 4.0 to 11.0% (and even to 16.0%) for unfilled resins and from 1.0 to 5.0% for filled resin composites [47—50].

In two-dimensional shrinkage, the bond strength can withstand the contraction forces because adhesion of the resin composite occurs on the flat (tooth) surface. This configuration provides a large free and unbonded surface, which enables the polymerizing and shrinking resin to flow across the free surface, whereby stresses occurring at the bonded surface are minimized. In three-dimensional shrinkage, the composite is bonded to two or more cavity walls. In this situation, the resin flow is limited or restricted, and the stresses generated at the bonded surface are becoming increasingly intense. The bonded surfaces then shrink differently from the unbonded surfaces.

Rapid polymerization processes induced by photocuring cause less resin flow than those, occurring in chemically cured resin composites [51]. Reduced rates of polymerization may allow the material to flow faster whereby the polymerization shrinkage stress becomes reduced in the sample [52]. The slower the flow, the greater the contraction stress. Two-step photocuring using different light intensities may reduce contraction stresses caused by limited flow [53].

ROLE OF AIR BUBBLES IN STRESS REDUCTION

The chemically cured resin composites are more porous owing to the incorporation of air bubbles on mixing. The air bubbles increase the internal free, unbonded surface area, which permits more resin to flow during polymerization, thereby decreasing the contraction-induced stress. The stress relief in thin resin layers is proportional to the amount of porosity in the resin. Increasing the content of air bubbles in a resin composite by 5% can reduce the stress level by approximately 50% [54]. Extensive air thinning of a bonding agent can result in oxygen inhibition of the polymerization of the adhesive layer, reducing the cure and lowering the bond strength.

ROLE OF WATER SORPTION IN STRESS REDUCTION

Resin composites can absorb water. Once a resin restoration is exposed to saliva or water, it can absorb water which causes a volumetric expansion that partially compensates for the polymerization contraction [43, 55-60]. Water sorption varies with cavity design and resin volume. Polymerization contraction is rapid and occurs on curing, while water-induced expansion is slower and may take days. The amount of stress relaxation due to water sorption may vary from one type of resin to another. Water sorbed can also erode the filler/matrix interface and soften the polymer network, thus reducing the strength, stiffness, and wear resistance [61]. The type of filler and the percent of filler loading also affect the extent of water sorption and subsequent stress relaxation of the resin [62]. The water uptake is difficult to determine because, simultaneously with the absorption of water, the ingredients of the merely partially cured resin and residual monomer may leak out. For that reason, water uptake cannot be measured by weighing the samples.

COMPUTER SIMULATION OF SHRINKAGE IN CURED DENTAL RESIN COMPOSITIONS

The shrinkage vector fields can be calculated by computer simulations of the elements [23, 24]. Figures 4a, b and c show computer simulations (MARC k 6.2, MARC Analysis Research Co., Palo Alto, CA, USA) of the pre-gel shrinkage vectors, post-gel shrinkage vectors, and total shrinkage vectors during "free shrinkage", respectively [24]. Direct experimental determination of the polymerization shrinkage vector directions is very difficult.

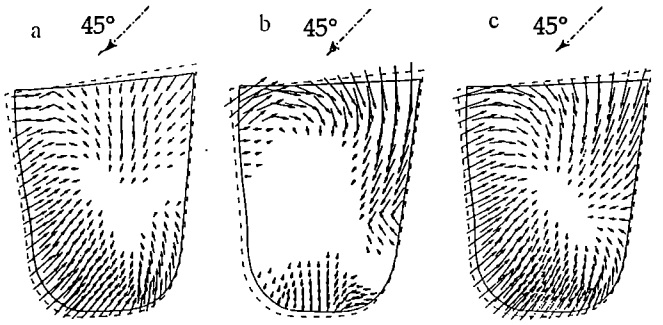


Fig. 4. Computer simulated shrinkage vector directions: (a) pre-gel shrinkage vectors, (b) post-gel shrinkage vectors, (c) total shrinkage vectors for a photocured composite; light incidence angle, 45° [24]

The tensile stresses formed during the polymerization contraction can be calculated by means of the finite element analysis [42, 63].

POLYMERIZATION SHRINKAGE OF (METH)ACRYLATE MONOMERS

(Meth)acrylate polymers have been very useful in numerous dental and other biomedical applications. Methyl

methacrylate exhibits a high polymerization shrinkage (~20% by volume) [64, 65], which very much limits the applications of poly(methyl methacrylate) in dentistry. Table 1 lists the density and volume shrinkage (S_V) data for poly(*n*-alkyl methacrylate)s. The polymerization volume shrinkage decreases as the number of carbon atoms in the side chain *n*-methacrylate is increased (Fig. 5) [14, 66].

T a b l e 1. Density of *n*-alkyl methacrylate monomers and polymers and their volume shrinkage (S_V, %) [66]

Ester	Density, g/cm^3		Shrinkage S_V, %
	monomer	polymer	
Methyl	0.939	1.190	21.00
Ethyl	0.909	1.119	18.76
Propyl	0.902	1.060	14.90
Butyl	0.889	1.055	15.73
Hexyl	0.880	1.010	12.87
Octyl	0.883	0.971	9.06
C_{12}	0.866	0.945	8.36
C_{13}	0.872	0.957	8.88
C_{16}	0.858	0.934*)	8.14

*) Amorphous polymer.

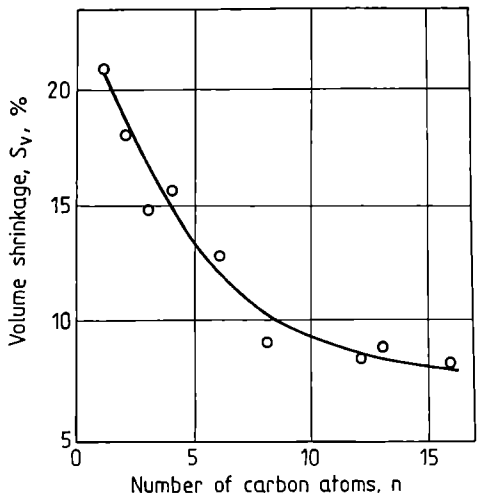


Fig. 5. Volume shrinkage (S_V, %) of n-alkyl methacrylates as a function of the number of carbon atoms (n) in the side chain [66]

T a b l e 2. Volume shrinkage (S_V) formed during polymerization of diacrylate and dimethacrylate monomers [15]

EG units in monomer	Monomer	S_V, %	Monomer	S_V, %
0	—	—	MMA	15.0
1	EGDA	12.7	EDGMA	15.1
2	DEGDA	11.1	DEGDMA	13.8
3	TrEGDA	11.7	TrEGDMA	12.0
4	TeEGDA	8.3	TeEGDMA	10.3
9	PEG(400)DA	8.0	—	—

Monomer abbreviations: EGDA — ethylene glycol diacrylate, DEGDA — diethylene glycol diacrylate, TrEGDA — triethylene glycol diacrylate, TeEGDA — tetra(ethylene glycol) diacrylate, PEG(400)DA — poly(ethylene glycol (400) diacrylate), MMA — methyl methacrylate, EDGMA — ethylene glycol dimethacrylate, DEGDMA — di(ethylene glycol) dimethacrylate, TrEGDMA — tri(ethylene glycol) dimethacrylate, TeEGDMA — tetra(ethylene glycol) dimethacrylate.

The volume shrinkage (S_V) of crosslinked poly(meth)acrylates prepared by polymerization of various difunctional acrylates and methacrylates is shown in Table 2 [15]. The S_V ranges from 8 to 13%. The monomers containing a lower number of ethylene glycol (EG) units between the two acrylic groups exhibit a maximum S_V. As the number of EG units increases, the S_V progressively decreases. This indicates that the monomers having shorter chain lengths form the most highly crosslinked materials. The diacrylates also show lower S_V than the corresponding dimethacrylates. In the series of dioldimethacrylates:

$$CH_2{=}C(CH_3){-}CO{-}O{-}(CH_2CH_2O)_n{-}CO{-}(CH_3)C{=}CH_2 \quad (I)$$

n = 4—12

co-polymerized with 2,2-bis[4-(2-hydroxy-3-methacryloyl--oxypropoxy)-phenyl]propane (Bis-GMA) at various ratios, the S_V decreased as the number of EG units "n" was increased [67, 68]. The density and volume shrinkage (S_V) data for Bis-GMA-based dimethacrylates are shown in Table 3.

T a b l e 3. Density and volume shrinkage (S_V) of Bis-GMA based dimethacrylates [66]

Monomer	Density, g/cm^3		Shrinkage S_V, %	Conversion, %
	monomer	polymer		
2,2-bis-4-[2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane	1.175	1.237	5.01	47
2,2-bis-4-[2-methacryloyloxyetoxy)phenyl]propane	1.121	1.200	6.58	59

The rate of shrinkage follows the rate of polymerization. However, for some monomers like tetra(ethylene glycol) diacrylate (TeEGDA) the rate of shrinkage at-

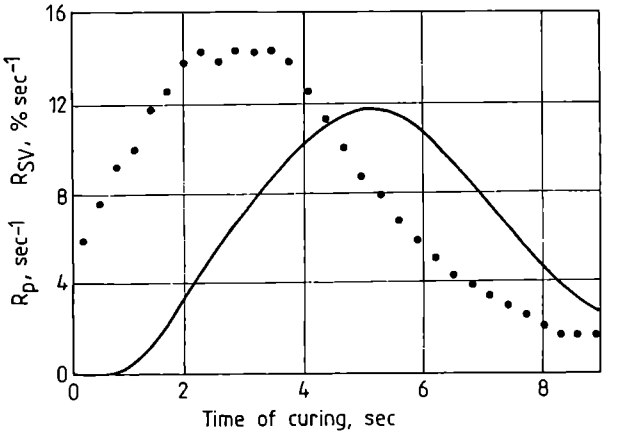


Fig. 6. Rate of polymerization (R_p, sec^{-1}) (continuous curve) and rate of shrinkage (R_{SV}, % sec^{-1}) (dotted curve) for TeEGDA [69]

tains maximum earlier than does the rate of polymerization [69] (Fig. 6). This discrepancy is a measurement error rather than the correct result.

With multifunctional (meth)acrylates the volumetric shrinkage lags behind the rate of polymerization [64, 70—72], because the polymerization reaction requires the monomer or single polymer branches to be mobile whereas shrinkage requires a concerted movement of the entire system. This shrinkage lag makes the polymerizing medium reach a higher conversion at a higher reaction rate [6, 73—74]. Higher reaction rates can be achieved by using an increased light intensity and/or and increased initiator concentration.

POLYMERIZATION SHRINKAGE OF COMPOSITES LOADED WITH FILLERS

Increasing the filler loading can significantly reduce shrinkage [20, 75]. The amount of shrinkage varies with filler type and its configuration, based upon filler's density and surface area. Inert fillers, which exhibit no dimensional change during the polymerization and curing processes, replace the dimensionally unstable resins. Filler contents in commercially produced dental resin fillings can be as high as 80% (Table 4) [2].

T a b l e 4. Names and composition of commercial dental composites [2]

Composite	Matrix	Average filler size, mm	Filler volume, %	Manufacturer
Heliomolar radiopaque	Bis-GMA + methacrylates	0.04	65—67	Vivadent, Schaan, Liechtenstein
Helioprogress	Bis-GMA + methacrylates	0.04	64	Vivadent
Silux	Bis-GMA + TEDMA	0.04	44	3M, St. Paul, MN, USA
Prisma APH	Urethane modified Bis-GMA	1	77—79	De Trey, Konstanz, Germany
Colténe brilliant dentine	Bis-GMA + TEDMA + methacrylate	0.5	77—78	Colténe AG, Allstalten, Switzerland

Bis-GMA = 2,2-bis-[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane.

In the absence of specific interactions between the filler and the fluid, the shrinkage ratio (ΔS) of the filled monomer can be expressed as follows [20]:

$$\Delta S = (1 - X)S_V \quad (1)$$

where: *X is the volume ratio of solid filler to monomer, S_V is the volume shrinkage of the cured resin [1].*

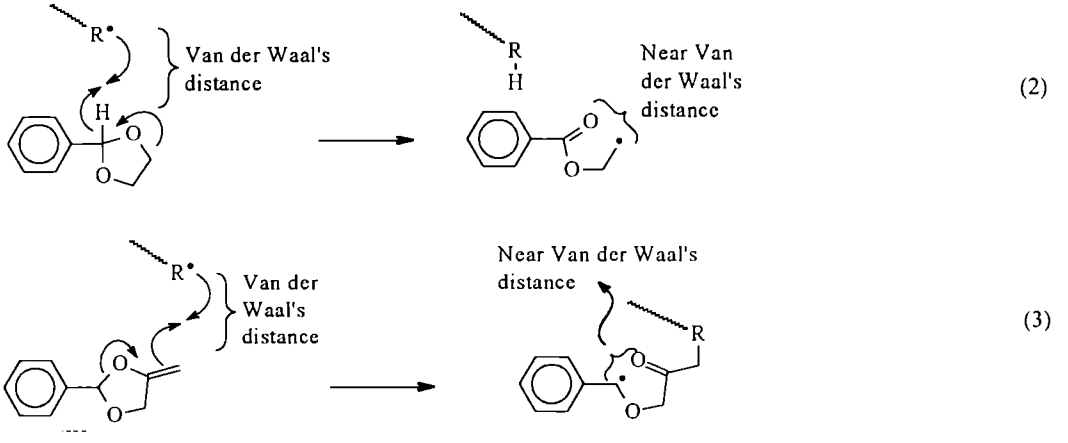
By equation (1), $\Delta S \Rightarrow 0$, if $X \Rightarrow 1$.

REDUCING OF SHRINKAGE BY ADDING PREPOLYMERS

Prepolymers have also been used to reduce shrinkage. A "prepolymer" is a viscous, medium-molecular-weight version of its solid, high-molecular-weight counterpart. A prepolymer is made by polymerizing the monomers to a viscous, but still liquid, stage prior to gelation and then terminating the polymerization process. The prepolymer is added to the base monomer mix to form a low to moderate viscosity solution which then can be polymerized to completion and cured. Since the prepolymer has already been partially polymerized, it will exhibit less shrinkage in photocuring.

FREE RADICAL RING-OPENING POLYMERIZATION

To counteract the shrinkage caused when chain growth polymerization occurs, monomers capable of free radical ring-opening polymerization have been designed [75—78]. Ring-opening monomers have the potential for polymerization with less volume change than non-cyclic (meth)acrylic monomers. During ring-opening polymerization of dioxolanes volume contraction is offset as some covalent bonds are ruptured to give near Van der Waals bond distances (Scheme I).



Scheme I

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Received 24 III 2000.