

Application of Diol Dimethacrylates in Dental Composites and Their Influence on Polymerization Shrinkage

DARIUSZ BOGDAL, JAN PIELICHOWSKI, ADAM BORON

Department of Polymer Chemistry and Technology, Politechnika Krakowska, ul. Warszawska 24, 31-155 Krakow, Poland

Received 6 February 1997; accepted 10 June 1997

ABSTRACT: Diol dimethacrylates (DD) that possess long aliphatic chains were incorporated into the conventional dental resin mixtures (e.g., BIS-GMA and TEGDMA) in order to reduce the polymerization stress and shrinkage of final copolymers. It was found that the polymerization shrinkage of the standard copolymer (60 mol % BIS-GMA and 40 mol % TEGDMA) could be reduced even by 20% when TEGDMA is substituted by a long aliphatic diol dimethacrylate. These phenomena can be attributed to the low miscibility of BIS-GMA and DD, which causes long aliphatic chains of DD to remain in coil form in a reaction mixture. The coils can be unwound and expand as a result of the formation of covalent bonds during polymerization and thus reduce the polymerization shrinkage. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2333–2337, 1997

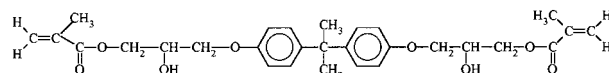
Key words: aliphatic diol dimethacrylates; BIS-GMA; TEGDMA; polymerization shrinkage; dental materials

INTRODUCTION

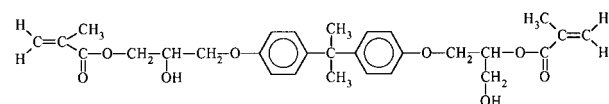
The dental restorative materials are based on various methacrylate monomers and oligomers.^{1–3} Investigations into this group of compounds were begun as early as the 1940s. During these years methyl methacrylate was applied. However, the initial filling materials had several serious defects. They were of insufficient technical quality to replace fluoride-containing silicate cements, gold, and ceramics. The main reason for this fact is the high polymerization shrinkage of methyl methacrylate. The fillings fell out easily, and moreover, the conversion of monomer was low (i.e., about 75%).² The rest of the monomer, which as a compound of low formula weight, can easily diffuse out. It is well known that methacrylic monomers are toxic, allergic, and mutagenic, especially for the pulp.^{2,3}

Since the development of composite resin re-

storative materials by Bowen in 1962,⁴ the production of polymers for dental application has increased rapidly. More than 100 commercially produced monomers have been used by private companies to prepare dental composites.^{5,6} They consist of an organic matrix in which inorganic filling particles are imbedded. The polymerizable material provides about 95% by weight of the organic portion, which itself amounts only to 10–30% by weight of the composite, the rest being inorganic fillers. The main component of the organic part is BIS-GMA:



Linear BIS-GMA
(bisphenol A diglycidylether dimethacrylate)



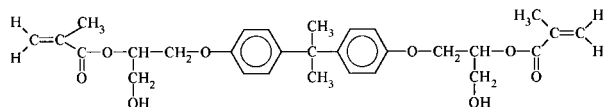
Branched BIS-GMA

Correspondence to: D. Bogdal.

Journal of Applied Polymer Science, Vol. 66, 2333–2337 (1997)

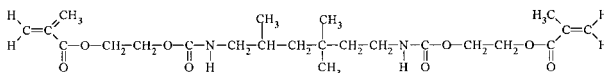
© 1997 John Wiley & Sons, Inc.

CCC 0021-8995/97/122333-05



Double branched BIS-GMA

In some modern composites another base monomer was applied:



"UEDMA"

The name UEDMA is currently reserved for compounds composing the urethane groups and methacryloyl groups.

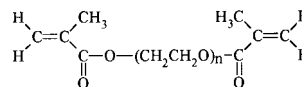
BIS-GMA is the most often used in restorative materials. The main advantage of this compound is low polymerization shrinkage, which is equal to 6.4% in comparison with 24.8% for methyl methacrylate. A composite that contains BIS-GMA possesses a satisfactory strength owing to the existence of an aromatic segment and good adhesion to the adjacent enamel. This base monomer has also some disadvantages. The most important is the presence of OH groups.⁷ As a consequence, the monomer shows high viscosity and sorption of water. The other disadvantage is the inability to purify the final product of synthesis BIS-GMA by crystallisation and distillation.

The investigations towards improving the materials for restorative dentistry based on the polymer matrices are still carried on. The lifetime for anterior polymeric restorative materials is about 8 years, but for posterior materials is often not longer than 2–4 years. In comparison with traditional dental amalgams, which have the time of use of about 10–20 years, this seems to be a very short period.^{1,3} In the last 15 years the questions about mercury release from amalgams fillings and the concern about toxicity of mercury have raised. This led to the necessity of replacing them with nontoxic materials, for example, polymer composite resins. As an interesting piece of news it can be said that in Sweden the application of amalgams is forbidden as of 1997.

DISCUSSION

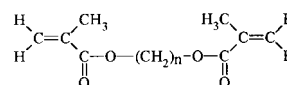
For the sake of high viscosity of BIS-GMA we have to add reactive diluent monomers of low viscosity. The glycol dimethacrylates are commonly

used to make the appropriate consistence of the organic portion of the restorative materials. In mixtures with BIS-GMA, 30–50% by weight of them is applied. In his first composite, Bowen applied methyl methacrylate,⁴ but it was very quickly replaced with ethylene glycol dimethacrylate. At present, triethylene glycol dimethacrylate can be analyzed in the most commercially manufactured restorative materials.



n = 1: EGDMA; n = 2: DEGDMA; n = 3:
TEGDMA; n = 4: TTEGDMA

As the other monomers of low viscosity, diol dimethacrylates are used:



n = 4 - 12

The next demand that has to be fulfilled is the value of polymerization shrinkage. It should not exceed 0.2–2% for restorative materials.² The phenomenon of shrinkage has not been eliminated by manufactures yet. The dentists also have their demands for easy handling of composite pastes. The application of inorganic fillers and high molecular monomers can reduce shrinkage to some extent, but because of the high viscosity, low molecular dilutents have to be added. The latter ones cause more curing shrinkage than the large molecules of BIS-GMA. As a result of volume decrease, a gap is formed between the wall of the cavity and the filling material. This gap is easily accessible for bacteria, which can initiate biodegradation processes, and the remains of food what cause secondary caries. The adhesion between walls and filling material becomes worse. There is another effect that is caused by polymerization shrinkage. A big stress is present within the material. The polymer matrix can be damaged and the microcracks can appear during the time of use.

The polymerization shrinkage has two main causes: (1) the molecules of monomer are placed in the some distances from one to another, which are called Van der Waals' radiuses. The monomer units in polymer are linked with the covalent bonding, which is about $\frac{1}{3}$ the Van der Waals' ra-

dius. In connection with this fact, the value of shrinkage that occurs during polymerization depends on the conversion of the monomer. (2) The change in entropy and the relative free volume of monomer and polymer. The latter one is determined by the packing efficiency of the macromolecules. Thus crystalline polymers are packed more closely than the noncrystalline ones.

For these reasons the polymerisation shrinkage cannot be avoided for methacrylate monomers. However, the monomers that polymerize with the increase of volume exist. The expansion of volume is achieved by the ring-opening process.⁸ The problem exists in obtaining adequate curing of these compounds under clinical conditions.

RESULTS

The shrinkage as a result of polymerization is of a great concern today. Our idea was to incorporate dimethacrylates with long aliphatic chains into the conventional dental resin mixture of BIS-GMA and TEGDMA.

To investigate the influence of dimethacrylates with aliphatic chains on the shrinkage of their copolymers with BIS-GMA and TEGDMA, we synthesized six diol dimethacrylates as well as the two traditional monomers (BIS-GMA and TEGDMA).⁹ The diol dimethacrylates and glycol dimethacrylates are carried out using two main methods.¹⁰ The first one is transesterification between methyl methacrylate and the higher diols or glycols with constant evaporation of the methanol. This method has one serious disadvantage. The product always contain about 20–30% of the diol or glycol monomethacrylates. The usage of monomers containing at least two double bonds became a rule in dental applications because only they have a chance to build in polymer network when the conversion of the monomer is low. The second one is reaction between methacryloyl chloride and diol or glycol. Obtaining esters according this procedure, we have to use very unpleasant and dangerous thionyl chloride, which finally contaminates the product.

The base monomer BIS-GMA is carried out from bisphenol-A diglycidyl ether and methacrylic acid according to the following mechanism¹¹:

1. Initiation: activation of acid by amine

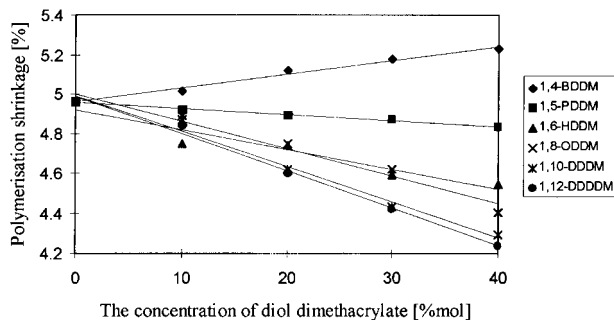
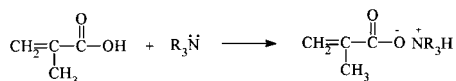
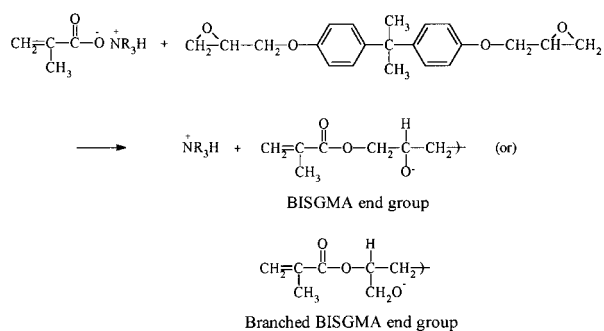
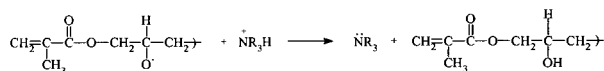


Figure 1 The relation between the polymerization shrinkage of homopolymer and the number of methylene groups in diol dimethacrylate.

2. Transfer:



3. Deactivation: Reaction of alkoxide anion with the deactivated amine, regenerates the catalyst in the reaction



The volumetric shrinkage of resins was determined using Archimedes' law.

The diol dimethacrylates and the mixtures containing 60% mol of BIS-GMA as well as various concentrations of TEGDMA and aliphatic dimethacrylates were cured in glass molds by the addition of 1% by weight benzoyl peroxide. The samples were heated up to 70°C over a period of 4 h, up to 85°C for 1 h, up to 100°C for 1 h, and up to 120°C for 2 h.¹²

The weight of the cured resin (W_c) was determined using a hydrostatic balance after removal from the mold and following trimming of the flash. Each specimen was weighed three times and the mean value was used as the weight of the specific specimen. The volume of uncured resin (V_{ur}) present in the mold prior to curing was calculated as follows:

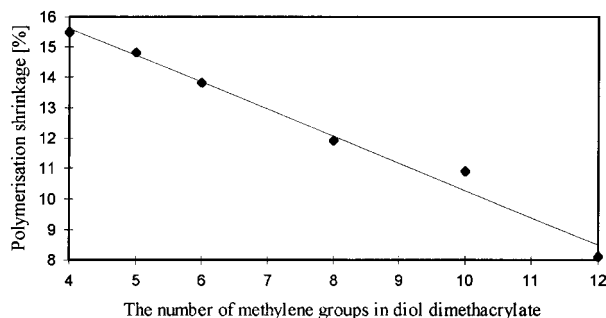


Figure 2 The relation between the polymerization shrinkage of the copolymers (60% mol BIS-GMA and 40% of the mixture of TEGDMA and DD) in the dependence on the number of methylene groups in diol dimethacrylate (DD).

$$V_{ur} = W_c/D_u$$

where D_u is the density of the uncured resin.

The weight of the cured resin was determined while it was suspended in distilled water (W_{rw}) at a specified temperature. The difference in weight readings between W_c and W_{rw} represents the weight of water displaced by the resin (W_w). The volume of this displaced water (V_w) was determined as follows:

$$V_w = (W_c - W_{rw})/D$$

where D is the water density at the measured temperature.

This is also equivalent to the volume of the cured resin (V_{cr}). The amount of volumetric shrinkage (V_s) can be now determined as follows:

$$V_s = V_{ur} - V_{cr}$$

The results of the experiments are presented at the Figures 1, 2, and 3.

While analyzing these figures it can be noticed that polymerization shrinkage of the homopolymers of diol dimethacrylates diminishes linearly with the number of methylene groups at the monomer (Fig. 1). It can be explained by the decrease of the concentration of double bonds with the increase of molecular weights of diol dimethacrylates. As it is well known, a lower concentration of double bonds causes a lower polymerization shrinkage of starting mixture.

For copolymers containing 60% mol BIS-GMA, TEGDMA, and the same concentration of various diol dimethacrylates, the relations above are exponential (Fig. 2). This means that the polymerization shrinkage of the copolymers diminishes expo-

nentially with the number of methylene groups in diol dimethacrylates. The exponential character of the relations increases with the concentration of diol dimethacrylates in copolymer containing 60% mol of BIS-GMA and 40% mol of the mixture of TEGDMA and diol dimethacrylate. For the concentration 10% mol of diol dimethacrylates the relations are almost linear, whereas for the copolymers containing 60% mol of BIS-GMA and 40% mol of TEGDMA the relation has the strongest exponential character (Fig. 2).

As it was shown, the polymerization shrinkage of the copolymers containing 60% mol of BIS-GMA and 40% mol of diol dimethacrylate could be reduced even by 1% in comparison with the standard mixture of 60% mol of BIS-GMA and 40% mol of TEGDMA, which is applied in dental restorative materials.

The volumetric shrinkage of the standard copolymers of 60% mol of BIS-GMA and 40% mol of TEGDMA is 4.96% (Fig. 3). However, the volumetric shrinkage of the homopolymer of TEGDMA is lower than the homopolymer of 1,6-hexanediol dimethacrylate and other higher dimethacrylates. The shrinkage of copolymers of 60% mol of BIS-GMA and 40% mol of the mixture of TEGDMA–diol dimethacrylate decreases linearly when the concentration of diol dimethacrylate increases (Fig. 3).

The situation is only different for the copolymers of BIS-GMA, TEGDMA, and 1,4-butanediol dimethacrylate, and the volumetric shrinkage increases linearly with concentration of the dimethacrylate. Even though 1,5-pentanediol dimethacrylate has significantly lower molecular weight than TEGDMA, the polymerization shrinkage of the copolymers of BIS-GMA, TEGDMA, and 1,5-pentanediol dimethacrylate are lower than for the standard copolymer of BIS-GMA–TEGDMA.

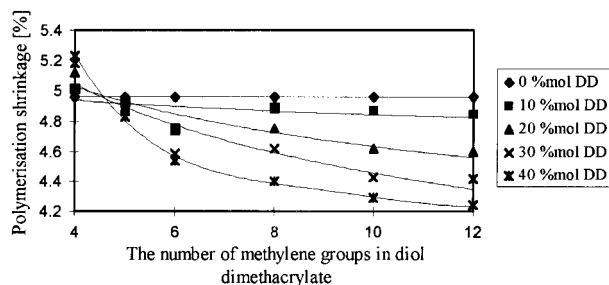


Figure 3 The relation between the polymerization shrinkage of the copolymer and the concentration of diol dimethacrylate and TEGDMA in copolymers containing 60% mol BIS-GMA and 40% of the mixture of TEGDMA and diol dimethacrylate.

These two examples, 1,5-pentanediol and 1,6-hexanediol dimethacrylates, indicate that monomers that are more hydrophobic and less miscible with BIS-GMA than glycol dimethacrylates (i.e., TEGDMA) can reduce the volumetric shrinkage of dental restorative materials.

The lower miscibility of diol dimethacrylates with long hydrophobic aliphatic chain results in coiled chain structure of the diols in the polymerization mixtures. The coiled chain can unwind during the polymerization process, reducing the stress of material and volumetric shrinkage.

This effect is more significant for higher diol dimethacrylates (1,8-octanediol, 1,10-decanediol, and 1,12-dodecanediol), but in this case the lower polymerization shrinkage can be explained by the lower concentration of double bonds in the mixture of monomers before the polymerisation processes.

SUMMARY

Diol dimethacrylates possess long, coiled chains that can unwind as a result of copolymerization with the traditional resins. The unwinding can then help to control the stress during shrinkage and also volumetric shrinkage. The dimethacrylates with aliphatic chains are more hydrophobic than dimethacrylates of glycols. Thus, they are less miscible with BIS-GMA. The miscibility of dental monomers has to be controlled. If the chain has a very good polymer-solvent interaction, it will tend to unwind when mixed with the resin before it cures. This condition is not desired. It is expected that the chain unwinds only as a result of pulling by the formation of covalent bond. Therefore, as it was shown, monomers on the edge of miscibility (i.e., long-chain aliphatic diol dimethacrylates) are desired.

PROCEDURES

We obtained diol dimethacrylates and triethylene glycol dimethacrylate in a one-step reaction by direct esterification.

A 250 cm³ three-necked bottomed flask, fitted with an efficient mechanical stirrer, a thermometer, and a Dean-Stark's trap with a reflux condenser was charged with *n*-alkyl diol (0.25 mol), fresh distilled methacrylic acid (0.5 mol), hydroquinone (1 g), 96% H₂SO₄ (2 cm³), and *n*-heptane (50 cm³). The reaction vessel was placed in a heating mantle and refluxed until the quantitative amount of water was collected in the Dean-Stark's

trap (3–6 h). The product was cooled and the solvent was evaporated under vacuum. The raw ester was placed in a separate funnel and washed three times with a 10% solution of NaOH, and then twice with a distilled water. The final product was dried over magnesium sulphate. Yield: 68–81%.

The lowest value of yield was when TEGDMA was carried out. The reason for this fact is higher density of this compound, which is similar to the density of water, and its higher hydrophilic properties.

Synthesis of BIS-GMA was carried out in three-necked round bottomed flask with an efficient mechanical stirrer, a thermometer, and a condenser. A fresh distilled methacrylic acid and EPIDIAN-6 (this is an epoxy resin containing about 95% diglycidyl ether bisphenol-A) in the stoichiometric proportions, 100 ppm hydroquinone and 1% by weight of *N,N*-dimethyl-*p*-toluidine as a catalyst was placed in the flask. The mixture was heated up to 60°C. The reaction was carried out until the peak at 917 cm⁻¹ almost disappeared. This peak is assigned to the terminal epoxy group. The final product was analyzed with the aid of FTIR and NMR methods.

REFERENCES

1. I. E. Ruyter, in *Posterior Composite Resin Dental Restorative Materials*, G. Vanherle and D. C. Vanherle, Eds., Peter Szule Publishing, Utrecht, 1985, 109.
2. L. A. Linden, *Proc. Indian Acad. Sci.*, **105**, 405 (1993).
3. E. Jodkowska, Med. Tour Press International, Wydawnictwa medyczne, Warszawa, 1993.
4. R. L. Bowen, U.S. Pat. 3 066 112 (1962).
5. J. F. Rabek, *Photodegradation of Polymers*, Springer Verlag, Berlin, 1996.
6. W. Spahl, H. Budzikiewicz, and J. Fresenius, *Anal. Chem.*, **350**, 684 (1994).
7. C. L. Davidson, in *Posterior Composite Resin Dental Restorative Materials*, G. Vanherle and D. C. Vanherle, Eds., Peter Szule Publishing, Utrecht, 1985, p. 61.
8. W. D. Cook, *J. Dent. Res.*, **59**, 800 (1980).
9. D. Bogdal, A. Boron, and J. Pielichowski, *Polimery*, **41**, 469 (1996).
10. M. Gibas and B. Szapska, *Pol. J. Appl. Chem.*, **93**, 277 (1993).
11. M. S. Sheela, K. Tamarasely, V. Kalliyana Krishnan, and S. N. Pal, *J. Appl. Polym. Sci.*, **42**, 561 (1991).
12. M. Atsuta and D. T. Turner, *Polym. Eng. Sci.*, **22**, 438 (1992).