*Article*

# Shrinkage Characteristics of Experimental Polymer Containing Composites under Controlled Light Curing Modes

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**Abstract:** The adsorption of polymethylmethacrylate polymer of different molecular weight at the aerosil/ethyleneglycol- or 1,3 butanediol-dimethacrylate interfaces was determined to provide microstructured networks. Their structural characteristics were determined to be controlled by the amount of polymer initially supplied to the system. The sediment (the settled phase) characteristics, determined as a function of the polymer concentration and the rate of the polymerization shrinkage determined for composite resins, obtained by extrusion of the sediment after centrifugation, were found to be correlated. The specific role of the adsorbed polymer was found to be differently perturbed with the supplementary supply of dimethacrylate based monomer additives. Particularly, the bisphenol A dimethacrylate that generated crystals within the sediment was found to impede the shrinkage along the crystal lateral faces and strongly limit the shrinkage along its basal faces. Addition of ethyleneglycol- or polyethylene-glycoldimethacrylate monomers was determined to modify the sedimentation characteristics of the aerosil suspension and the shrinkage properties of the composites. Finally, the effects of stepwise light curing methods with prolonged lighting-off periods were investigated and found to modify the development and the final values of the composite shrinkage.

**Keywords:** composite light curing; resin shrinkage; aerosil/polymer/dimethylacrylate based monomer resin; structured crystal-like composite; stability of polymer/aerosil suspension

## 1. Introduction

The aim of the studies developed since 2004 was to investigate the shrinkage features of experimental composite resins containing the polymethylmethacrylate (PMMA) polymer. This polymer strongly interacts with the silica oxide surface of aerosil and becomes adsorbed at the silica/methylmethacrylate interfaces [1]. The objective was to strongly control the interfacial figures of the adsorbed polymethylmethacrylate polymer by supplying various amounts of polymer and/or additional surface active monomers with the final objective to reduce the resin shrinkage during light curing of the composite. The usual way to reduce polymerization contraction and optimize the resin performance has been the incorporation of organic and inorganic fillers of various morphologies and sizes [2]. To solve the filler-matrix incompatibility [3], the filler/matrix interactions were modified by treatment with functionalized or bare silane coupling agents. Finally, these investigations provided the following information. The performance of some composites cannot be definitely attributed to a certain morphology or size of the filler or to specific filler/matrix interactions [4–6]. All these characteristics interact in a complex way and finally give rise to composites presenting reasonable mechanical properties. It is usually accepted that the best resin reinforcement results from the incorporation at the optimal dose of particles of small size that are homogeneously distributed within the resin [7].

This assertion contravenes some conclusions derived from a recent numerical simulation study. Lusti *et al*. determined the rigidity of the composite material not to depend on the homogeneous or inhomogeneous distribution of the filler within the resin [8]. Conversely, incorporation of aggregated particles was shown to induce better wear resistance. Agglomerated particles may be viewed as being the result of covalent binding of silica nanoparticles that are known under the generic term of aerosils. Since aerosil particles that are dispersed in methylmethacrylate or ethyleneglycoldimethacrylate monomer exerted strong interactions with the polymethylmethacrylate molecules, the suspension characteristics were profoundly modified. Addition of polymethylmethacrylate instantaneously induced aerosil aggregation, which resulted in agglomerate formation. Since 2006, the investigations were extended to a more complex matrix containing a small amount of bisphenol A dimethacrylate [9]. In this system, the filler developed a colloidal crystal-like arrangement that was determined to be responsible of an unexpected small degree of shrinkage [10]. Some features of the polymethylmethacrylate modified resin are affected by the addition of small amounts of ethyleneglycoldimethacrylate monomers of different molecular weight. Since changes in the monomer composition might potentially control the polymer adsorption characteristics, it was interesting to investigate how such chemical modification of the resin formulation will have negative or positive influence on the composite shrinkage characteristics. Since 2009, this objective was carried on with the determination of the shrinkage evolution during and/or after light curing. Interest focused on resins composed of 1,3 butanedioldimethacrylate as the major monomer and ethyleneglycoldimethacrylate or polyethyleneglycoldimethacrylate as the secondary monomer. In the present investigation, the shrinkage was continually measured with the CCD line scan sensor and the lens belonging to it was calibrated for the determination of the rate and the extent of the polymerization contraction of composites. The resin was extruded to form a cylinder of 2.5 mm diameter and 5–6 mm length, then deposited onto a glass blade and put on the device. Light curing was performed either

quasi-continuously or stepwise, thus combining periods without lighting of variable duration. Intensity of curing light was constant during lighting periods [11]. This procedure constituted an alternative way with regard to some methods of the literature. Earlier work has shown that soft-start cure of a resin composite gave rise to reduced polymerization contraction of the restoration because of stress relief by flow [12]. Soft-start cure may be brought about by the so-called pulse-delay cure, where the polymerization was initiated by a short flash of light followed by a waiting time of several minutes before the final cure was performed [13–15]. Another soft-start technique involved so-called step-curing, where a reduced intensity of curing light was used during the first part of the polymerization period. These techniques have been found to not induce appreciable alteration of mechanical properties and degree of monomer conversion [16–22]. However, the pulse-cure method may give rise to a different structure of the polymer although degree of conversion and hardness in the dry state were not affected by the curing method [23]. In the present context it was interesting to determine if the initial period of lighting in the stepwise regime is able to freeze the network structure characterized by such a high crosslink density.

## 2. Experimental Section
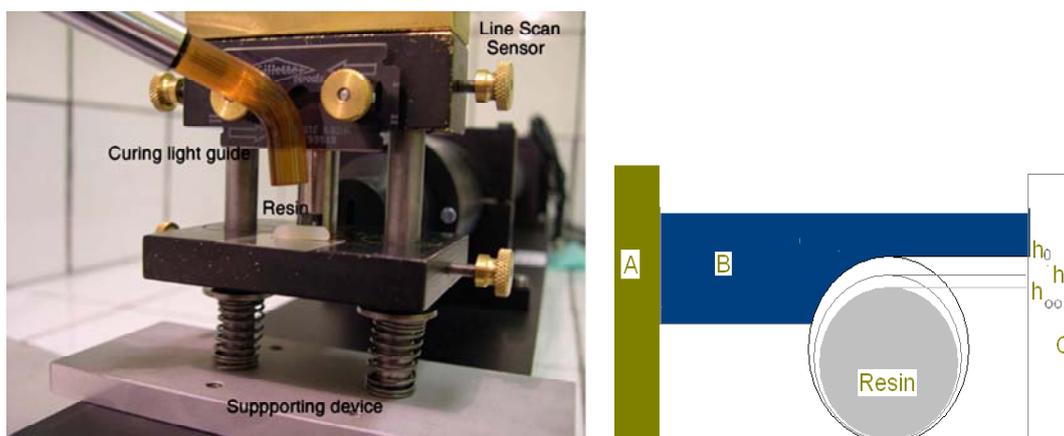
### 2.1. The CCD Line Scan Sensor

The CCD ZS16D line scan sensor (H-D Rudolph GmbH, Germany) especially built to register digital signals over a maximal height of 1,600 μm was employed for the determination of the polymerization contraction of composites. The object to be measured was located between the line scan sensor and the illuminator and cast a shadow (Figure 1(left)). It was illuminated homogeneously and constantly from behind and was imaged to a CCD in the line scan sensor (200 images per second). Since the object is larger than 1,600 μm, the supporting device was vertically adjusted in order to scan the upper limiting zone of the object (Figure 1(right)). The CCD recognized the distribution of brightness in the measuring range and transformed it into an analog video signal. A comparator compared the video signal with a trigger level and thus formed an image of the object to be measured in the form of a digital signal. From the top levels $h_0$ and $h$ of the resin cylinder determined before and during polymerization, and the top level $h_\infty$ determined at the end of the polymerization run, which were determined with a precision of 0.1 μm, the variation with time of the resin shrinkage is given by $1 - (D/D_0)$ according to the relationship:

$$1 - (D/D_0) = (h_0 - h)/(D_\infty + (h_0 - h_\infty))$$

where $D_\infty$ is the composite diameter determined at the end of the polymerization run with a digital caliper rule having an accuracy of 0.01 mm. To get the highest accuracy in the determination of the top levels of the resin during polymerization, the measurements were made during successive intervals of 10 s when the light of the visible light curing unit was off. The duration of the lighting periods was of 20 s. All results relative to the rate of the relative composite contraction $1 - (D/D_0)$ were represented as a function of the analysis time (s). The precision of the shrinkage determination was ±0.0001 [24]. The reliability of the present method may be valuably compared to that of the digital image correlation and other photographic methods presented in [25,26]. Methods using dilatometers and pycnometers were also employed [27] and a critical analysis of these different methods has been

given in [28]. For all methods, volume change during cure is directly proportional to the degree of polymerization. The advantage of the present line scan technique over other methods resides in the possibility to instantaneously record the sample height, and thus to derive the shrinkage rate.

**Figure 1.** (**Left**) Photograph of the line scan sensor (H-D Rudolph GmbH, Germany), the guide of the visible light curing unit, and the cylindrical resin deposited on the supporting device. (**Right**) Schematic representation of the device: (**A**) represents the light emitter, (**C**) is the captor, and (**B**) the parallel light beam illuminating the top zone of the Resin. $h_0$, h and $h_\infty$ are the lower detected levels of the beam in the presence of the resin at time 0, at a given time t and at the end of the polymerization run.



*2.2. The Filler/Matrix Dispersion*

Polymethylmethacrylate (PMMA) polymers of molecular weight of $10^5$ and $5.5 \times 10^5$ Da were synthesized in the laboratory and extensively purified in order to eliminate residual monomers. A sample of molecular weight equal to $1.5 \times 10^6$ Da was of commercial origin. The experiments were carried out at 25 °C. PMMA was chosen as the polymeric material to aggregate the fractal silica aerosils. Among the different fractal powders already employed as fillers in composite resins, the OX 50 sample (50 $m^2/g$) (Evonik-Degussa GmbH) was selected due to the strong interaction existing between the polymer and the silica oxide dispersed in the methylmethacrylate or ethyleneglycoldimethacrylate, (1,3 butanedioldimethacrylate + bisphenol A dimethacrylate) and the polyethyleneglycoldimethacrylate monomers of molecular weight equal to 330 and 875 Da. All these monomer products were from Sigma-Aldrich and used as received. The relative height of the sediment resulting from the addition of PMMA to the aerosil suspension was determined by taking as reference the initial height $H_0$ of the dispersion in the glass vial prior to addition of the PMMA polymer. The measurements of the sediment height at different times and at the end of settling $H_\infty$ were carried out and determined on the basis of photographic reproductions, which allowed a precision in $H_\infty/H_0$ equal to ±0.01.

Camphorquinone was used as photoinitiator and dimethylaminoethylmethacrylate as accelerator at concentrations of 0.25 and 0.3% by weight, respectively [29]. The photoinitiator and the accelerator were added to the methylmethacrylate monomer and the mixture was gently homogenized to obtain powder dissolution in the dark. The relative doses of the three constituents were fixed to add the

camphorquinone/amine initiator system in a reproducible way. The advantage of dissolving the photoinitiator and the accelerator in the methylmethacrylate monomer was to impede any polymerization reaction within this mixture.

An amount of 0.5 g aerosil suspended in 15 mL monomer was sonicated for 5 min in order to generate a true solid/liquid interface. Then a given amount of the PMMA dissolved in the methylmethacrylate monomer was added to the aerosil dispersion. The use of methylmethacrylate monomer made it possible to stock the solute polymer for long times. The different samples of the polymer/aerosil/monomer mixture differed by the polymer dose, which was varied from 0 to 10 mg PMMA/0.5 g aerosil.

Aliquots of 1.5 mL of the silica/PMMA/monomer dispersion were taken from the system and transferred into Eppendorf tubes. For all resins, the Eppendorf tubes were centrifuged at 6,000 rpm for 20 min. Then, the supernatant liquid was evacuated and the settled phase was extruded throughout a cylindrical tube of diameter equal to 2.5 mm to form a cylindrical resin of diameter very close to 2.5 mm, which was immediately transferred onto the line scan sensor device to carry out the correspondent measurements.

*2.3. The Light Curing System*

The wavelength of the light emitted by the curing unit (Aurys, DegréK, France) was between 400 and 520 nm (1,650 mW/cm$^2$). The cross-sectional area of the light guide was equal to 5 mm and the distance between the line guide tip and the crystal was held constant near 5 mm. The curing method and operational condition induced a given unknown polymerization conversion that usually led to a time-independent shrinkage within a period of 200 to 300 s under conditions of quite permanent lighting In addition, the single initial lighting of 20 s activates a prolonged polymerization that is expressed by a prolonged linear shrinkage visible up to 70 to 100 s. This particular aspect is developed in Section 3.4.

**3. Results and Discussion**

The investigation of the effects of the polymer supplied to the more usual resin composed of filler and a mixture of monomers were carried out using PMMA molecules of different molecular weights. When the objective was to determine the influence of the single supply of polymer to the usual resin, PMMA molecules of high molecular weight were selected in order to enhance the polymer effect. The high and the medium molecular weight polymers were also used when the effect of a crystal-like arrangement was investigated under the effect of addition of the particular bisphenol A dimethacrylate monomer. Polymers of low molecular weight were employed to investigate the effect of non-structuring additives. It was "reasonably" supposed that the influence of these additives could be better evidenced when the PMMA was of lower molecular weight.

Table 1 presents the chemical composition of the main systems which were examined for their shrinkage ability and/or their sediment characteristics. Clearly, the main monomer systems were changed by supplying various monomer additives in order to modify the silica/polymer interactions with the objectives to determine such effects on the shrinkage ability.

**Table 1.** Main systems and chemical composition *.

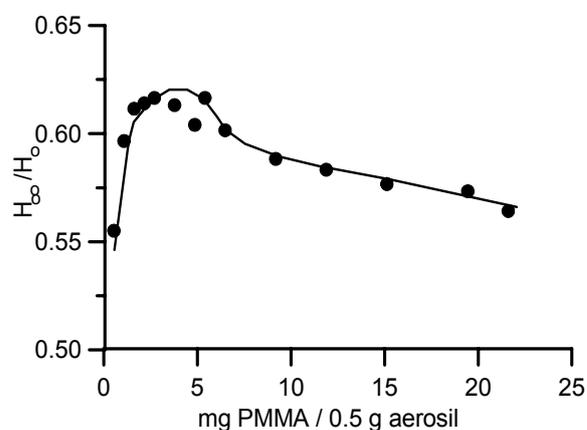| PMMA Mol. Weight | Basic Monomer System | Additives | Figures |
|---|---|---|---|
| $1.5 \times 10^6$ | methylmethacrylate | - | 2, |
| $1.5 \times 10^6$ | ethyleneglycol dimethacrylate | - | 3,4 |
| $1.5 \times 10^6$ | bisphenol A dimethacrylate + 1,3 butanedioldimethacrylate | - | 6(a), 7 |
| $1.5 \times 10^6$ | bisphenol A dimethacrylate + 1,3 butanedioldimethacrylate | polyethyleneglycol dimethacrylate (875) | 6(b), 8 |
| $1.5 \times 10^6$ | bisphenol A dimethacrylate + 1,3butanedioldimethacrylate | polyethyleneglycol dimethacrylate (330) | 6(c), 6(d) |
| $10^5$ | 1,3 butanedioldimethacrylate | - | 8 |
| $10^5$ | 1,3 butanedioldimethacrylate | ethyleneglycoldimethacrylate | 8, 9 |
| $10^5$ | 1,3 butanedioldimethacrylate | polyethyleneglycoldimethacrylate (330) and (875) | 8,9 |
| $5.5 \times 10^5$ | 1,3 butanedioldimethacrylate | - | 10, 11 |

* The amount of polymer (mg/0.5 g aerosil) supplied to the system is indicated in the figure caption.

The experimental results developed in Subsection 3.1 show how the PMMA molecules of molecular weight equal to $1.5 \times 10^6$ Da being adsorbed at the silica oxide/methylmethacrylate interface modify the stability characteristics of the suspended colloid firstly, and influence the rate of shrinkage of the aerosil/ethyleneglycoldimethacrylate resin, secondly. Results developed in Section 3.2 show to what extent the addition of a secondary monomer modifies the shrinkage features of the basic monomer systems (see column 2 in Table 1). Results presented in Section 3.3 show the influence on the sedimentation process and on the composite shrinkage resulting from the addition of some different monomer additives. Finally, results presented in Section 3.4 show the influence of prolonged switch-off-phases on the shrinkage development of the resin.

*3.1. Correlation between the Amount of PMMA Supplied and the Instability Characteristics of the Aerosil/PMMA/Methylmethacrylate Dispersion*

The high values of the relative height of the sediment appearing in Figure 2(left) indicate that supplying PMMA (Mw = $1.5 \times 10^6$ Da) to the dispersed silica suspension led to formation of colloidal aggregates whose sediment height at equilibrium depended on the amount of PMMA supplied to the aerosil dispersion. Even at 25 mg polymer/0.5 g of silica, the polymer supplied did not stabilize the dispersed silica particles. Obviously, the highest level occurred for supply of 4 mg PMMA. When before settling, the position of the vial was modified in order to generate different forms of the settled phase, these forms were stable over months. This certainly corresponded to the realization of a real scaffold containing the aggregated silica particles as portrayed in Figure 2(right).

**Figure 2.** Representation of the relative height of the sediment as a function of the amount of polymethylmethacrylate (PMMA) polymer supplied to 0.5 g aerosil suspended in 15 mL methylmethacrylate monomer (**left**). Representation of two unusually stable forms of settled sediment for the system (0.5 g aerosil/15 mL methylmethacrylate/4.32 mg PMMA) corresponding to the maximal $H_\infty/H_0$ value (**right**).



## 3.2. Correlation between the Amount of PMMA Supplied and the Shrinkage Rate of the Aerosil/PMMA/Ethyleneglycoldimethacrylate Resin

The extent of shrinkage at 20 °C reported in Figure 3 in terms of $1 - (D/D_0)$ as a function of time corresponded to the polymerization of the resin enclosing bare aerosil (a), and of the resin enclosing PMMA polymer coated aerosil at the dose of 4.32 mg PMMA/ 0.5 g aerosil (b). The maximal rates of shrinkage expressed in percentage per min as determined from the initial slope of the variation of $1 - (D/D_0)$ as a function of time are 1.80 (a), and 1.20 (b), respectively. Experiments (a) and (b) correspond to successive lighting periods of 20 s. interrupted with lighting off periods of 10 s. and display initial linear increase of the shrinkage.

It was therefore interesting to explore the domain of the PMMA doses below and above the dose generating the maximal aggregation and corresponding to the most efficient inter-particle bridging. Figure 4 summarizes the values of the shrinkage rate as a function of the polymer dose: maximal height of the settled phase (see Figure 2(left)) and lower rate of polymerization shrinkage are obtained for the same polymer dose of 4.32 mg PMMA/0.5 g aerosil.

The correlations existing between the rate of polymer shrinkage of the extruded resin (the composite) and the compactness of the settled phase were expressed by taking into account the bulk conformation of the PMMA molecule and the structure of the fractal silica, as well as their relative sizes. The scaffold-like structure and stability were examined in the light of results relative to the agglomeration of fractals [30]. The agglomeration of fractal aggregates was investigated with the objective to determine the average number of inter-aggregate connections when two aggregates stick together. The average number of inter-aggregate connections generated by the aggregate agglomeration was determined to be close to 2.2 and independent of the agglomerate mass, whereas it is equal to 1 for a doublet of spheres. This may further explain why the incorporation of fractals within the resin induces stronger mechanical properties as derived from the numerical study [8].

**Figure 3.** Representation of $1 - (D/D_0)$ as a function of time for ethyleneglycoldimethacrylate resins enclosing particles without added PMMA polymer (**a**) (small and large black symbols refer to duplicate experiments), and for a polymer dose of 4.32 mg PMMA polymer added to 0.5 g aerosil (**b**).
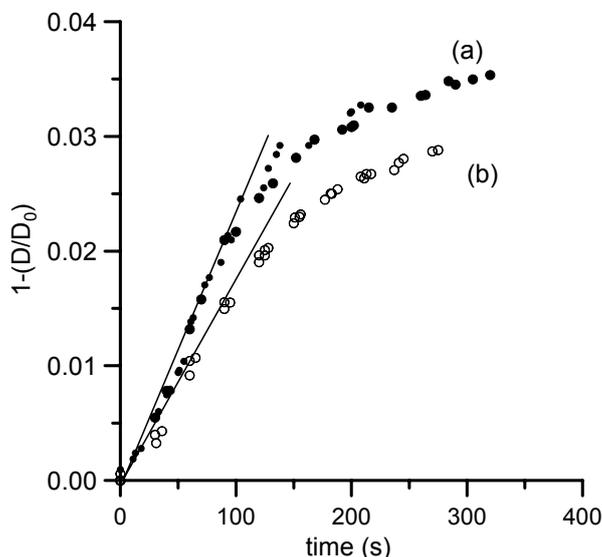


**Figure 4.** Representation of the rate of shrinkage of composite resins reinforced with aerosil coated at different degrees as a function of the amount of PMMA supplied to the systems.
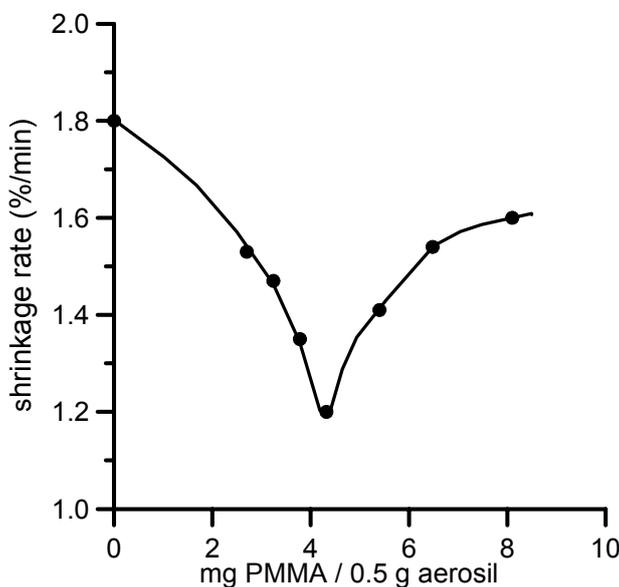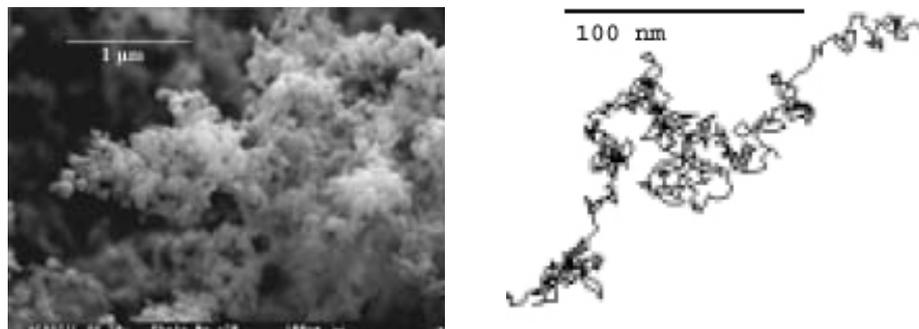


Figure 5 proposes a representation of the relative sizes of the polymer (in solution) and the aerosil (in the suspension). It is clearly shown that the interaction of the polymer backbone with the fractal aggregate may be able to generate agglomerates characterized by a large number of 3D-structures, sizes and compactness, all of these features also depending of the degree of "surface" coating.

**Figure 5.** Snapshots of the aerosil OX 50 (**left**) [31] and of the linear polymer of molecular weight close to $1.5 \times 10^6$ Da (**right**).



The formation of a polymer scaffold is more easily realized when the solid surface concomitantly bears polymer free and polymer coated surface areas [32]. Destabilization of the aerosol particles thus results from the adsorption of chain segments belonging to the same polymer on the surface of two neighbor particles, which builds a polymer bridge. The real situation corresponding to the highest sediment is not easily portrayed but leads to the following comments:

- small loops are formed if the inter-particle distance extremely low surface coating. Then, adsorbed polymer may be relatively inefficient when the adsorbed chain is expected to oppose the polymer shrinkage by spring effects.
- large loops are built if the inter-particle distance within the doublet is great due to the higher surface coating. The resulting configuration of the adsorbed polymer is more efficient when the adsorbed chain opposes polymer shrinkage. The amplitude of the shrinkage partly depends on the resistance being progressively opposed by the polymer springs when two particles get closer with the progress of the polymerization.
- the ideal situation within the doublet is small, as resulting from the seems to be reached when the sediment agglomerates large individual aggregates also containing large voids initially filled with monomers.

### 3.3. Influence of the Colloidal Crystal-Like Arrangement of Polymethylmethacrylate Bonded Aerosil Particles on the Shrinkage of Composite Resins

The new resin system was realized by replacing the ethyleneglycoldimethacrylate monomer by a mixture of monomers prepared at 42 °C by dissolving 5 g of bisphenol A dimethacrylate in 12 mL of 1,3 butanedioldimethacrylate. This solution is stable at 25 °C. The molecular weight of the PMMA was $1.5 \times 10^6$.

In the short term, the colloid/PMMA aggregates appeared as an homogeneously settled phase and the mixture of 1,3 butanedioldimethacrylate and bisphenol A dimethacrylate as a clear supernatant. However, after 3 weeks, more compact small platelets and residual aggregates could be observed within the settled phase as revealed by the image of a thin film cast from the system (Figure 6(a)). Alternately, similar figures of the heterogeneous sediment were obtained when the settled phase was perturbed by slow agitation or by inserting a needle within. Finally, when the system is fully left at rest for months, new figures appeared, also represented in Figure 6.
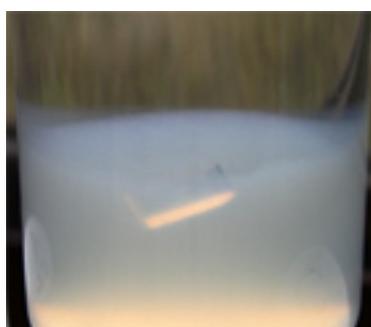
- Figure 6(b) represents a unique crystal growing within the settled sediment. 1g of polyethyleneglycoldimethacrylate of molecular weight equal to 875 Da was added to the basic resin. This supply led to obtain the transparent crystal as depicted in Figure 6(e).

- Figure 6(c,d) represents opaque crystals that were obtained in the absence and in the presence of the other monomers. For instance, the addition of 1 g of the polyethyleneglycol dimethacrylate monomer of molecular weight equal to 330 Da produced an opaque crystal. The opaque crystal as took from the settled phase is also shown in Figure 6(e).

From the macroscopically heterogeneous sediment corresponding to Figure 6(a,c), three composite resins were realized by the usual extrusion method.

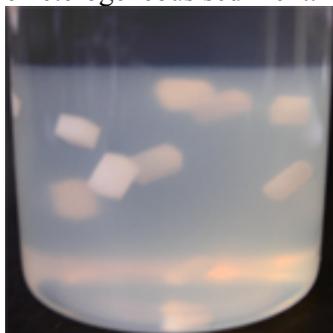**Figure 6.** Representation of different figures of the settled sediment.



(**a**) opaque aggregates within the heterogeneous sediment.

(**b**) the single clear crystal suspended in the sediment.

(**c**) numerous opaque platelets in the sediment.

(**d**) a few opaque crystals in the sediment phase.
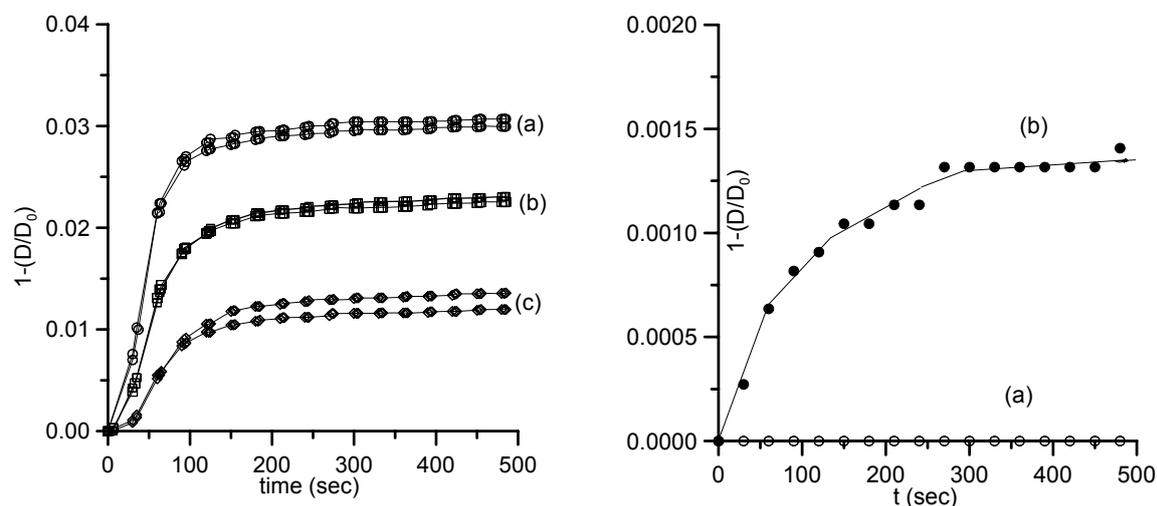
(**e**) the clear and opaque crystals.
(Printing is Arial 12)

(**f**) the clear macroscopic crystal.
(the breadth of the basal face is equal to 7.45mm)

The first composite was realized using the whole deposit recovered after centrifugation at 6,000 rpm for 20 min of the settled phase. The second composite was extruded using the deposit recovered after centrifugation of the opaque aggregates isolated from the settled phase (Figure 6(a)). The third composite was extruded after centrifugation of the opaque platelets isolated from the sediment shown in Figure 6(c). The last composite was directly polymerized as small crystals taken from the sediment. Figure 6(f) is an example of this class of crystals and constitutes a sample of unusually large size. The shrinkage of the three composites and the crystals is represented in Figure 7(left,right) respectively, as a function of time.

**Figure 7.** Representation of $1 - (D/D_0)$ as a function of time for the aerosil/(1,3 butanedioldimethacrylate + biphenol A dimethacrylate) system in the presence of 1.62 mg PMMA/0.5 g aerosil: the platelet system (a); the aggregates (b), and the settled whole sediment (c). (The (a), (b) and (c) curves refer to duplicate experiments) (**left**). Representation of the polymerization shrinkage $1-(D/D_0)$ determined for crystals lying on the basal (a) or on the lateral face (b) (**right**).



The composite corresponding to the settled whole sediment sustained a shrinkage close to 3%, which is very comparable to that of systems realized with aerosil initially dispersed in the ethyleneglycoldimethacrylate monomers. Composites realized on the base of aggregates or platelets recovered and extruded after centrifugation sustained shrinkage close to 2.2 or 1.2%, respectively. Obviously, since the resin preparation method was not able to ideally separate the platelets and the aggregates from the whole system, the shrinkage determinations of these special systems were not reproduced with the expected precision. Nevertheless, the different resin preparation modes provided composites characterized by very different shrinkage behaviors. Essentially, the smallest shrinkage was obtained with the resin only realized with platelets. It is noticeable that extensive light curing did not increase the degree of shrinkage. In addition, the corresponding composite remained friable even under extended light curing conditions. Conclusively, when the portion of aggregates or platelets increased, and/or when the filler in the form of platelets replaced the amorphous aggregates, the degree of shrinkage notably decreases. It results that the small and large platelets and the crystal-like fillers should be characterized by an internal organization that opposed curing [10]. The internal organization was evidenced using atomic force microscopy and the limitations imposed to light curing by the structural organization of the crystal were evidenced by crystal curing experiments.

To realize photopolymerizable crystals, as usually camphorquinone was used as photoinitiator and dimethylaminoethylmethacrylate as accelerator. After supply of polymer at the different doses, these samples were held in the dark up to formation of crystals of size close to 2.5 mm. The determination of the polymerization shrinkage was done for crystals lying on the basal or on the lateral phase in order to evidence a possible heterogeneous organization of the crystal. Figure 7(right) shows the rate and extent of polymerization shrinkage for two clear crystals (composed of 0.5 g aerosil/12 mL 1,3 butanedioldimethylacrylate, 5 g bisphenol A dimethacrylate, 1 mL polyethyleneglycol dimethacrylate

and 1 g bisphenol A propoxylate diacrylate/3 mg PMMA). Each determination of the shrinkage was carried out on the crystal sample freshly taken out from the sediment. When the crystal was lying on the basal face, the line scan sensor allowed us to determine changes in the distance between the upper and the lower basal faces. The polymerization shrinkage is then equal to zero as reported in Figure 7(right). The increase of $1 - (D/D_0)$ tends to stabilize at 0.0015 when the crystal was lying on one of the lateral faces. This clearly indicates that the selective incorporation into the growing crystal of polymer and monomers around the aerosil aggregates and the crystal organization contribute to greatly impede the shrinkage. The absence of shrinkage between the two basal faces certainly results from the existence of a well-oriented monomer arrangement perpendicular to the basal faces that contravened polymerization. Conversely, the apparently low composite shrinkage observed between opposite lateral faces should result from a different organization of the aerosil/polymer/monomer system in the direction parallel to the basal faces, which not opposed the polymerization process, but strongly limited the volume contraction [34].

Incorporation of the bisphenol A dimethacrylate monomer additives, and occasionally the bisphenol A propoxylate diacrylate monomer in the resin based on 1,3 butanediol dimethacrylate confers to the composite the greatest stability against shrinkage and, unfortunately drastically limits the degree of polymerization conversion within these highly organized composites. These constraints are less marked when the heterogeneous phase is only present in the form of less structured aggregates, as shown in Figure 7(left)-a.

## 3.4. Influences of Various Monomer Additives, the Concentration and the Molecular Weight of the PMMA Molecule

The molecular weight of the PMMA molecule used in these experiments was equal to $10^5$ Da. The basic monomer was methylmethacrylate in the sedimentation experiments and 1,3 butanediol dimethacrylate in the light curing experiments. The monomer additives were ethylene glycol and polyethylene glycol of molecular weight equal to 330 and 875 Da.

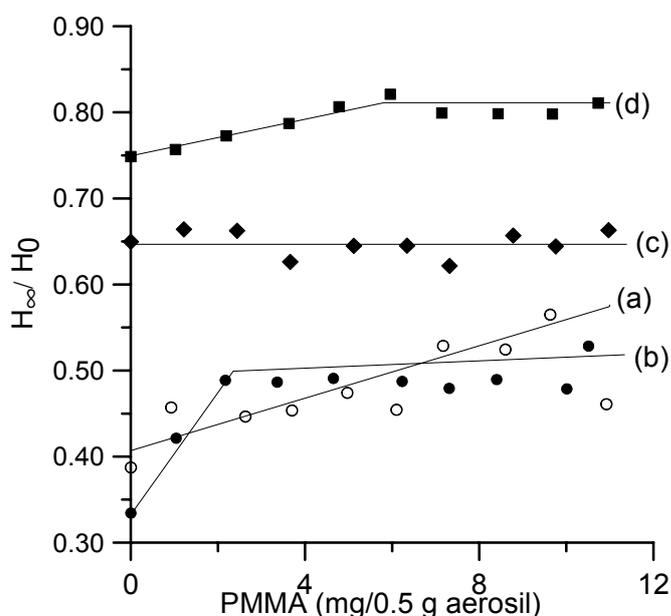3.4.1. Relative Sediment Height of the Composite Scaffold

After mixing of the aerosil and the monomers, different amount of PMMA were supplied to the system which was gently rotated to homogenize the colloidal suspension. Then, the systems were left at rest and the relative sediment heights $H_\infty/H_0$ were determined after one week.

The relative sediment heights were determined on the various vials containing various amounts of PMMA between 0 and 12 mg/0.5 g aerosil and the result is reported in Figure 8. The following comments are made:

- In the absence of any monomer additive and in the absence of PMMA, the relative sediment height is equal to 0.40 and linearly increases with the amount of polymer supplied. It should be noted that the conditions of optimal colloid destabilization are not yet reached for the supply of 12 mg PMMA.

- In the presence of 1 g ethyleneglycoldimethacrylate, the relative sediment height is equal to 0.34 in the absence of PMMA and linearly increases with the amount of PMMA supplied up to the maximal value of 0.50 which is reached near 2 mg PMMA.
- In the presence of polyethyleneglycoldimethacrylate of molecular weight equal to 330 Da, the relative sediment height is close to 0.65 and appears to be independent of the PMMA concentration.
- In the presence of polyethyleneglycoldimethacrylate of molecular weight equal to 875 Da, the relative sediment height is equal to 0.75 in the absence of PMMA and linearly increases with the amount of PMMA supplied up to the maximal value of 0.81 which is reached near 6 mg PMMA.

**Figure 8.** Representation of the relative sediment height $H_\infty/H_0$ as a function of the PMMA concentration (mg/0.5 g aerosil) in the absence (**a**) and in the presence of the monomer additive ethyleneglycoldimethacrylate (**b**), polyethyleneglycoldimethacrylate of molecular weight equal to 330 (**c**) and 875 (**d**), respectively.
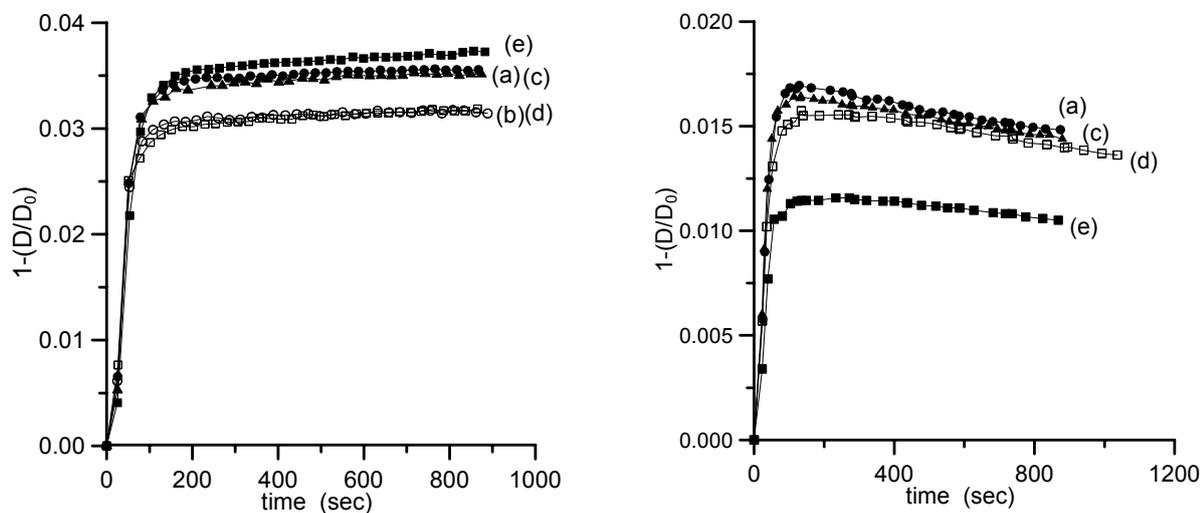


Therefore, in the two last situations, the destabilization process should be attributed partly to the PMMA molecule and partly to the polyethyleneglycoldimethacrylate additives which may compete with PMMA molecules in the adsorption process at the aerosil surface.

Values of $H_\infty/H_0$ determined in the absence of PMMA shows the strong influence of the polyethyleneglycoldimethacrylate additives while the supply of the ethyleneglycoldimethacrylate does not greatly perturb the stability characteristics of the aerosil/methymethacrylate system. Nevertheless, the presence of 1 g of ethyleneglycoldimethacrylate imposes a lower level of the initial deposit and, above the concentration of 2 mg PMMA/0.5 g aerosil, opposes the usual increase due to the PMMA molecule.

3.4.2. Curing Characteristics of the Composite Resin Containing PMMA of Molecular Weight $10^5$ Da

The resin cylinder was realized after centrifugation of the sediment and extrusion, and the light curing conditions were applied as usually, in the form of successive polymerization periods of 20 s and short interruptions allowing recording of the *h* values. Resin shrinkage are shown in Figure 9 (left). The supply of 10 mg PMMA to the aerosil/1,3 butanedioldimethacrylate system only slightly reduces the final shrinkage of the resin: $1 - (D/D_0)$ only varies from 0.035 to 0.031. This value of 0.031 is also reached when polyethyleneglycoldimethacrylate of molecular weight 330 Da is supplied to the PMMA/aerosil/1,3 butanedioldimethacrylate system. For the same system, the ethylene glycol dimethacrylate cancels the PMMA effect. It is noticeable that the ethyleneglycol or polyethyleneglycoldimethacrylate additives may (i) compete with the 1,3 butanediol dimethacrylate molecules in the polymerization process and (ii) modify the adsorption characteristics of the PMMA molecules at the aerosil surface

> **Figure 9.** Representation of the polymerization shrinkage $1 - (D/D_0)$ for composite
> resin realized in the absence of PMMA and without additive (**a**), in the presence
> of 10 mg PMMA/0.5 g aerosil without additive (**b**), and in the presence of 10 mg
> PMMA/0.5 g aerosil with 1 g of the monomer ethyleneglycoldimethacrylate (**c**),
> polyethyleneglycoldimethacrylate of molecular weight equal to 330 (**d**) and 875 Da (**e**),
> respectively: successive polymerization runs of 20 s (left) and a single polymerization run
> of 20 s (right).



Due to this complex involvement of the polymer and the additive in the PMMA adsorption and the polymerization process itself, a series of experiment was carried out to determine the time dependent shrinkage resulting from a single curing period of 20 s (see Figure 9 (right)). This procedure allows distinguishing between (i) the effect resulting from the additives on the PMMA adsorption figures, that are already fully established, and (ii) the effect resulting from the copolymerization of the dimethacrylate based monomers, that should be very limited at the low degrees of composite conversion compatible with the relatively small shrinkage.
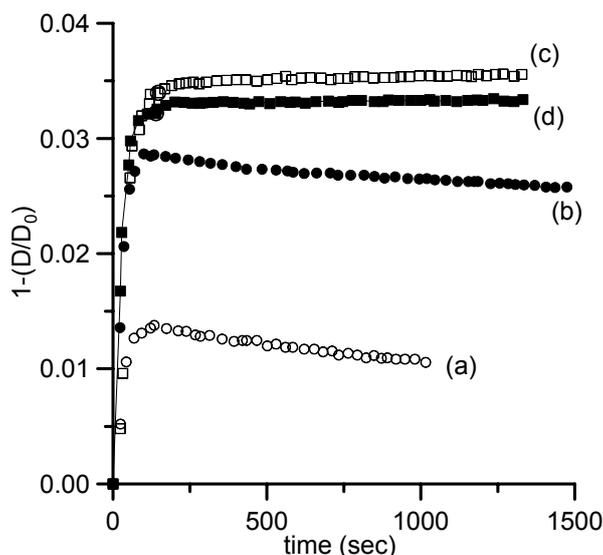
Three results of Figure 9(right) deserve to be analyzed:

- The shrinkage increases continuously up to 150 s despite the fact that the curing light is turned off after 20 s.
- The maximal shrinkage determined near 150 s decreases when the molecular weight of the additive increases. The effect is maximal for the polyethyleneglycoldimethacrylate of molecular weight 875 Da, whose adsorption characteristics on silica are the most favorable.
- Above near 150 s the shrinkage slowly decreases more or less at the same rate. At the low degree of composite conversion some viscous deformation is still available and residual stress is evacuated with the progressive swelling of the composite resin.

3.4.3. Curing Characteristics of the Composite Resin Containing PMMA of Molecular Weight Equal to $5 \times 10^5$ Da

In the following experiments, curing was carried out with resins realized without monomer additives. The effects of the PMMA concentration and the curing conditions were determined and represented in Figure 10.

**Figure 10.** Representation of the polymerization shrinkage $1 - (D/D_0)$ for composite resin containing 5 mg (open symbols) and 10 mg PMMA/0.5 g aerosil (black symbols), respectively. Curing conditions were $1 \times 20$ s, (**a**,**b**) and $5 \times 20$ s, (**c**,**d**), respectively.
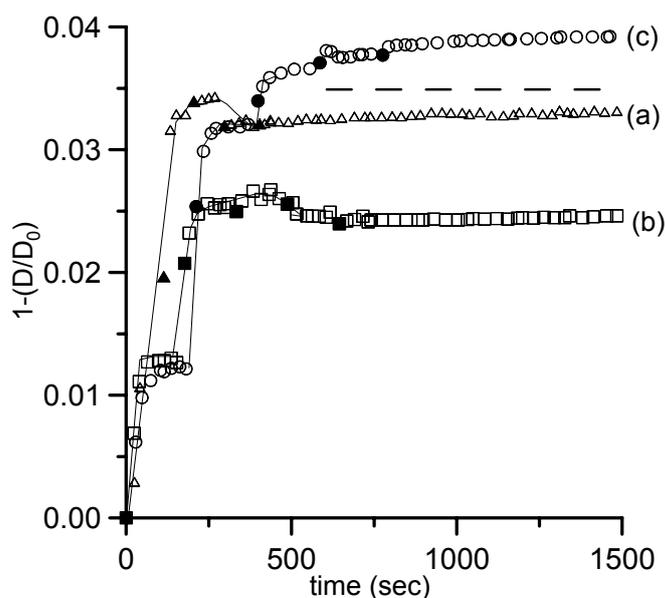


For experiments carried out with successive curing periods of 20 s, the resin shrinkage is slightly lowered when the PMMA concentration is equal to 10 mg PMMA/0.5 g aerosil in comparison to the system only containing 5 mg PMMA/0.5 g aerosil. The thicker adsorption layers on silica aerosil ensure limited shrinkage when the composite conversion is maximal. When a single curing period of 20 s is applied, the result is the inverse: PMMA layers of 5 mg PMMA/0.5 g aerosil stronger oppose the shrinkage than do layers of 10 mg PMMA/0.5 g aerosil. Actually, it is not possible to interpret the observed behaviors when the PMMA concentration was doubled. The conclusion is that when different amounts of polymer were supplied to the systems, the effects may be similar to the situation where the supply of the lower molecular weight additives modifies the interfacial characteristics of the PMMA adsorbed layers as the result of competitive adsorption.

*3.5. Shrinkage of the Composite Scaffold during Light Curing: Influence of the Stepwise Lighting Mode*

Curing experiments reported in previous Sections correspond to relatively simple processes. In one case, a single curing period of 20 s was applied to the resin and in other cases, curing was applied in the form of successive periods of 20 s while lighting was shortly interrupted to record the h values. The existence of the composite relaxation observed in the first case led to examine the time dependent shrinkage resulting from the succession of curing periods of 20 s and lighting-off periods of 1, 2 or 3 min. The experiments concerned resins containing PMMA of molecular weight equal to $5.5 \times 10^5$ Da at the concentration of 5 mg PMMA/0.5 g aerosil, without any supplementary additive.

**Figure 11.** Representation of the polymerization shrinkage $1 - (D/D_0)$ resulting from the stepwise lighting mode for composite resins containing 5 mg PMMA/ 0.5 g aerosil. The variable parameter was the duration of the lighting-off period: 1 min (**a**), 2 min (**b**) and 3 min (**c**), respectively. Black symbols correspond to the shrinkage values immediately recorded at the end of each lighting period of 20 s. The horizontal dashed line represents the maximal shrinkage value recorded for the quite continuous lighting of the composite.



Shrinkage developments represented on Figure 11 demonstrate the complexity of the leading phenomena. Clearly, the same PMMA adsorption figures characterize the resin tested in experiments (a), (b) and (c) on Figure 11. Since the beginning of the resin shrinkage should be identical as resulting from the firstly applied lighting-on period, the fate of the composite strongly deviates for lighting-off periods of 1, 2 and 3 min, respectively. In the first case—curve (a)—lighting-on periods rapidly lead to strong shrinkage that continues with engaging a fast relaxation within the subsequent lighting-off period. In the second situation—curve (b)—the shrinkage is relatively small and the third lighting-on period introduces an important composite relaxation which later decreases progressively. In the third situation—curve (c)—the lighting-on periods further led to enhanced shrinkage and relaxation processes of lower extent. It is noteworthy that the shrinkage corresponding to the maximal composite conversion that is determined for the quite continuous lighting of the composite in the experiment shown in Figure 10 (and represented by the horizontal dashed line in Figure 11) may possibly be

realized, either when the lighting-off period is smaller than 1 min or smaller than 3 min. In the first case, the relaxation processes are inhibited while in the second case, relaxation processes take the advantage. Periods of lighting-off larger than 3 min seem to induce larger shrinkage processes but it may be estimated that the composite conversion is unchanged.

## 4. Conclusions

The polymer was determined to exert a very perceptible influence on the rate of shrinkage, as well as on the absolute value of the contraction. These effects were attributed to the polymer adsorbed on the aerosil particles and to the relevant bridging phenomena. Bridging strongly stabilizes the aggregated fractal aerosil particles that build the scaffold.

Since in the first study the investigation focused on the single effect of the adsorbed polymer, the investigations were opened to determine the effects of supplementary additives like bisphenol A dimethacrylate (a resin structuring monomer) and other dimethacrylate based additives of different molecular weight. Results obtained on composite resins with bisphenol A dimethacrylate showed that this monomer is able to confer a high internal crystal-like organization of the composite. It was determined on crystals that even the monomers undergo a spatial rearrangement that inhibits polymerization in one direction and strongly limits the shrinkage in the other direction. Investigations relevant to systems containing supplementary monomers such as ethyleneglycoldimethacrylate or polyethyleneglycoldimethacrylate show that such additives concomitantly exert two effects. Firstly, they perturb the adsorption properties of the PMMA molecules as evidenced by the sedimentation experiments, and secondly some additives interfere in the polymerization process of the basic monomer by controlling the rate and/or extent of the volume contraction.

Al these effects were finally found to influence the time dependent composite shrinkage when periodic lighting-off periods were inserted during the light curing polymerization of the composite. The final shrinkage was found to depend on the durations of the lighting-off and lighting-on periods. The major conclusion is that the present investigation serves as a basis for further studies on these original composites containing fillers with tailor-made polymer-coatings.

## References and Notes

1.  Pefferkorn, A.; Haïkel, Y; Pefferkorn, E. Polymerization contraction of light-cured composite resins containing silica/polymethylmethacrylate bonded microstructured networks. *J. Colloid Interface Sci.* **2005**, *291*, 388–395.

2.  Ferracane, J.L. Resin composite—State of the art. *Dent. Mater.* **2011**, *27*, 29–38.

3.  Strobl, B. *The Physics of Polymer*, 2nd ed.; Springer: Berlin, Germany, 1997.

4.  Ruddell, D.E.; Maloney, M.M.; Thompson, J.Y. Effect of novel filler particles on the mechanical and wear properties of dental composites. *Dent. Mater.* **2002**, *18*, 72–80.

5.  Luo, J.; Seghi, R.; Lannuti, J. Effect of silane coupling agents on the wear resistance of polymer-nanoporous silica gel dental composites. *Mat. Sci. Eng.* **1998**, *C5*, 15–23.

6.  Luo, J.; Lannuti, J.J.; Seghi, R. Effect of filler porosity on the abrasionresistance of nanoporous silica gel/polymer composites. *Dent. Mater.* **1998**, *14*, 29–36.

7.  Ikejima, I.; Nomoto, R.; McCabe, J.F. Shear punch strength and flexural strength of model composites with varying filler volume fraction, particle size and silanation. *Dent. Mater.* **2002**, *19*, 206–211.

8.  Lusti, H.R.; Karmilov, I.A.; Gusev, A.A. Effect of particle agglomeration on the elastic properties of filled polymers. *Soft Mater.* **2003**, *1*, 115–120.

9.  Pefferkorn, A.; Pefferkorn, E.; Haïkel, Y. Influence of the colloidal crystal-like arrangement of polymethacrylate bonded aerosil particles on the polymerization shrinkage of composite resins. *Dent. Mater.* **2006**, *22*, 661–670.

10. Pefferkorn, A.; Maaloum, M.; Pefferkorn, E.; Haïkel, Y. Polymer induced crystal organization of composite resins. *Dent. Mater.* **2008**, *24*, 1647–1654.

11. Asmussen, E.; Peutzfeldt, A. Two-step curing: Influence on conversion and softening of a dental polymer. *Dent. Mater.* **2003**, *19*, 466–470.

12. Davidson, C.L.; Feilzer, A.J. Polymerization shrinkage and polymerization shrinkage stress in polymer-based restoratives. *J. Dent.* **1997**, *6*, 435–440.

13. Suh, B.I.; Feng, L.; Wang, Y.; Cripe, C.; Cincione, F.; de Rijk, W. The effect of the pulse-delay cure technique on residual strain in composites. *Compendium* **1999**, *2*, 4–12.

14. Kanca, J.; Suh, B.I. Pulse activation: Reducing resin-based composite contraction stresses at the enamel cavosurface margins. *Am. J. Dent.* **1999**, *12*, 107–112.

15. Sahafi, A.; Peutzfeldt, A.; Asmussen, E. Effect of pulse delay-curing on *in vitro* wall-to-wall contraction of composite in dentin cavity preparations. *Am. J. Dent.* **2001**, *14*, 295–296.

16. Silikas, N.; Eliades, G.; Watts, D.C. Light intensity effects on resin composite degree of conversion and shrinkage strain. *Dent. Mater.* **2000**, *16*, 292–296.

17. Uno, S.; Asmussen, E. Marginal adaptation of a restorative resin polymerized at reduced rate. *Scand. J. Dent. Res.* **1991**, *99*, 440–444.

18. Koran, P.; Kurschner, R. Effect of sequential versus continuous irradiation of a light-cured resin composite on shrinkage, viscosity, adhesion, and degree of polymerization. *Am. J. Dent.* **1998**, *11*, 17–22.

19. Yap, A.U.; Ng, S.C.; Siow, K.S. Soft-start polymerization: Influence on effectiveness of cure and post-gel shrinkage. *Oper. Dent.* **2001**, *26*, 260–266.

20. Bouschlicher, M.R.; Rueggeberg, F.A.; Boyer, D.B. Effect of stepped light intensity on polymerization force and conversion in a photoactivated composite. *J. Esthet. Dent.* **2000**, *12*, 23–32.

21. Mehl, A.; Hickel, R.; Kunzelmann, K.H. Physical properties and gap formation of light-cured composites with and without softstartpolymerization. *J. Dent.* **1997**, *25*, 321–330.

22. Rueggeberg, F.A.; Caughman, W.F.; Chan, D.C.N. Novel approach to measure composite conversion kinetics during exposure with stepped or continuous light-curing. *J. Esthet. Dent.* **1999**, *11*, 197–205.

23. Asmussen, E.; Peutzfeldt, A. Influence of pulse-delay curing on softening of polymer structures. *J. Dent. Res.* **2001**, *80*, 1570–1573.

24. To quantify the reliability of the technique, the standard deviation of the shrinkage of various commercial resin samples (Estellite, Tetric Flow, Inten-S, Tetric Ceram, Tetric Ceram HB) was measured and determined to be 0.0002 and 0.0001 for shrinkage within 0.0087 and 0.0355, respectively. The diameter of the cylindrical resins was varied from 0.73 to 2.30 mm and the shrinkage was found to be independent of the resin diameter. The shrinkage values were found to be very close to the values indicated by the manufacturer.

25. Furukawa, T.; Arakawa, K.; Morita, Y.; Uchino, M. Shrinkage Deformation Measurements of Dental Restorative Resin Composites. In *Proceedings of the XIth International Congress and Exposition*, Orlando, Florida, USA, 2–5 June 2008.

26. Haider, M.; Hubert, P.; Lessard, L. Cure shrinkage characterisation and modeling of a polyester resin containing low profile additives. *Composites Part A* **2007**, *38*, 994–1009.

27. Lai, J.H.; Johnson, A.E. Measuring polymerization shrinkage of photo-activated materials by a water-filled dilatometer. *Dent. Mater.* **1993**, *9*, 139–143.

28. Shah, D.H.; Schubel, P.J. Evaluation of cure shrinkage measurement techniques for thermosetting resins. **2010**, *29*, 629–639.

29. Lalèque, N.; Giral, L.; Montginoul, C.; Schue, F.; Sledz, J. Les matériaux composites utilisés en odontologie, de véritables œuvres d'art de chimistes. *L'actualité chimique* **1992**, 283–296.

30. Tatek, Y.; Stoll, S.; Pefferkorn, E. Internal cohesion of agglomerates. II. An elementary approach for assemblies of weakly agglomerated 3-d clusters. *Powder Technol.* **2001**, *115*, 226–233.

31. Database—Progra2. Project ICARE; Université de Lille: Lille, France, September 2010.

32. Napper, R.H. *Polymeric Stabilization of Colloid Dispersion (Colloid Science)*; Academic Press: New York, NY, USA, 1983.

33. Pefferkorn, E. The Cohesion of Fractal Agglomerates: An Elementary Numerical Model. In *Particle Breakage*; Salman, A.D., Ghadiri, M., Hounslow, M.J., Eds.; Elsevier: London, UK, 2007; Handbook of Powder Technology, Volume 12, pp. 741–791.

34. Pefferkorn, A.; Maaloum, M.; Haïkel, Y.; Pefferkorn, E. Anisotropic crystal growth in aerosil/polymethylmethacrylate systems dispersed in dimethacrylate monomers. *J. Colloid Interface Sci.* **2007**, *311*, 45–51.