Packable resin의 미세경도와 경화수축

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┌─ 국문초록 ─

  Packable resin은 아말감을 대신할 수 있을 것이라는 기대와 함께 상용화되었다. 이런 packable resin은 종래의 hybrid resin과는 달리 필러함량이 높고 분포가 더 조밀하다. 본 연구에서는 높은 필러함량이 packable resin의 미세경도와 경화수축에 미치는 영향을 조사하고 그 결과들을 hybrid resin에서 얻은 것들과 비교하였다. 그 결과 packable resin은 hybrid resin에 비하여 보다 높은 미세경도를 보였는데 본 실험에 사용된 레진들은 종류에 관계없이 그들의 미세경도가 필러함량(vol%)과 상관관계가 있었다. 또한 packable resin은 hybrid resin에 비하여 훨씬 적게 경화수축 하였는데 관찰된 경화수축과 필러함량 사이에는 역상관관계가 있었다.

  주요어 : Packable resin, 미세경도, 경화수축

I. Introduction

Packable composites are the new class of resin composites. They have a high viscosity, and a high filler load and distribution make them comparable to the conventional hybrid composites. Claims regarding these materials are that they undergo less polymerization shrinkage and they are able to substitute amalgam in stress-bearing posterior restorations. Like many composites, packable composite resins are light polymerizable. Polymerization is a process where the monomer molecules placed at 'van der Waals' radius converse into a polymer network of covalent bonds. A closer packing of the molecules leads to bulk contraction or polymerization shrinkage due to the shortening of the final polymer network[1]. The polymerization shrinkage is inherent in the monomer-based composites[2].

The pointed variables that influence polymerization shrinkage were the size of the monomer molecules, the volume of filler, the degree of polymerization, and the type of resin composites[3]. Polymerization shrinkage depended on the mixture of Bis-GMA and the amount of diluting monomers. Since each monomer has a different molecular weight, the difference of the type and polymerization chemistry will affect the polymerization process.

The filler volume fraction, filler size, and filler load level of the composites were in correlation with the material strength, elastic modulus, and fracture toughness[4,5]. A positive correlation between the microhardness (Hv) and inorganic filler content was reported[6]. Increased filler levels resulted in an increased microhardness value[7]. Fillers in composites are solid and free from contraction; nevertheless, since the volume of the filler determines the remaining volume of organic resin matrix, the magnitude of the polymerization shrinkage is also affected by the filler content.

To determine the degree of polymerization shrink-

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age, various devices have been utilized[8,9]. Since the determination of shrinkage, however, was based on the free shrinkage-strain measurements, the measurements of the composite linear shrinkage are quite varied[9,10].

As a result of polymerization shrinkage, the stress from shrinkage-strain can cause many clinical problems such as the opening of restoration margins that can result in microleakage, caries recurrence, debonding, and postoperative pain[11,12]. In addition to the polymerization shrinkage, cyclic temperature changes in the oral cavity according to eating, drinking, and breathing can affect the bond at the tooth-restorative interface and gap dimension due to the differences of thermal expansion[13,14].

The purpose of this study was to investigate the polymerization shrinkage and microhardness of packable composites. Conventional hybrid resins were also tested for comparison.

II. Materials and methods

For the study, two packable resins and two conventional hybrid resins were used and their characteristics were listed in Table 1. To measure the surface microhardness before and during the thermocycling process, a Vickers hardness tester (FM-7, FUTURE-TEC Inc., Japan) was utilized. Seven samples for microhardness from each resin product were prepared by placing the resin into an acrylic ring mold (7 mm in diameter and 1 mm in depth) and covered

with a thin glass slide. The glass slide was firmly pressed to ensure a flat surface. The sample was light polymerized with a 700 mW/cm² light intensity for 40 seconds. The prepared samples were kept in a dark container for 24 hours prior to taking the measurements.

1. Microhardness test

After 24 hours, the microhardness of the surface was measured using a hardness tester. Two indentations were made on the surface with a 200-g load and a 15-second dwell time. During the themocycling process, the measurements were performed repeatedly using the same samples after 2000 and 5000 cycles.

Each measurement was performed near the previously measured position after the removal of samples from the water bath and removing the remaining water. The measured samples were immediately immersed in the water bath and thermocycled between 4℃ and 60℃ with a dwell time of 30 seconds in each bath.

2. Polymerization shrinkage measurement

For the polymerization shrinkage measurements (n=5) during the light curing process, a linometer (RB 404, R&B Inc., Daejon, Korea) was utilized. This system is composed of a sample holder, curing light, shrinkage sensing part, software and comput-

Table 1. Characteristics of the packable resins tested in this study

| Material	Composition	Filler type (vol%*)	Filler content	Batch	Manufacturer
FP	Bis-GMA, Bis-EMA, UDMA	zirconia/silica	62	20030129	3M
PD	Bis-GMA, TEGDMA, EBADM	Ba-Al-borosilicate glass	52.5	310697	Kerr
SF	Urethane modified Bis-GMA	Ba-F-Al-borosilicate glass, silica	60.3	20227	Dentsply/Caulk
SN	Bis-GMA, Bis-EMA, TEGDMA	Ba-Sr-Al-borosilicate glass	51.1	MF542	Coltene/Whaledent

FP: Filtek P60; PD: Prodigy; SF: SureFil; SN: Synergy
* : According to the calculation of Braem et al[5].

er. The sample resin is located between the slide glass and aluminum disc on the sample holder. A teflon (polytetrafluoroethylene, PTFE) mold (1.5, 2.5, and 3.5 mm thickness with an inner diameter of 4 mm) was placed over the aluminum disc and the sample resin was transferred to the teflon mold. To facilitate the measuring process, Vaseline was coated slightly onto the disc. After filling the resin fully, the

teflon mold was removed. A slide glass was then secured over the resin. The probe of the curing light unit (CuringLight XL3000, 3M, St. Paul, USA) was in contact with the slide glass. Before the light curing, the initial position of the aluminum disc was set to zero. The light was irradiated from the unit with a 700 mW/cm^2 light intensity for 40 seconds. As the resin polymerized, it shrunk toward the light source and then the aluminum disc under the resin also moved toward the light source. The amount of disc displacement that occurred due to the polymerization shrinkage was auto scaled by the non-contacting inductive gauge for 300 seconds. The used shrinkage sensor is a non-contacting type and resolution is 0.1 μm with a 100 μm measuring range.

Table 2. Microhardness (Hv) for different thermocycling number

	0	2000 cycle	5000 cycle
Filtek P60	77.33±0.93	69.12±1.26	65.85±0.72
Prodigy	50.36±1.00	47.81±0.98	51.83±0.64
SureFil	67.05±0.72	60.96±1.63	59.78±1.33
Synergy	47.55±0.48	44.05±0.90	45.72±0.73
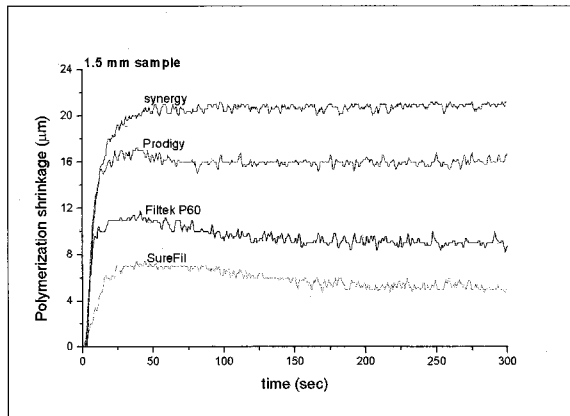
**Fig. 1.** The shrinkage profiles of 1.5 mm sample.
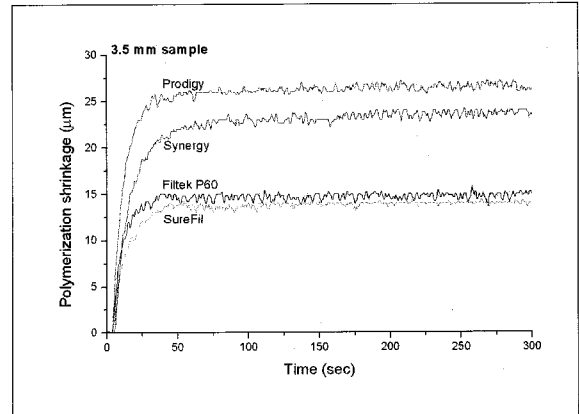
Fig. 2. The shrinkage profiles of 3.5 mm sample.

Table 3. Polymerization shrinkage (μm) for different thick samples

	Polymerization shrinkage (μm)		
	Sample A	Sample B	Sample C
Filtek P60	9.5±1.3	10.2±0.9	16.2±1.2
Prodigy	17.5±0.6	21.2±1.5	28.0±2.3
SureFil	6.0±0.8	12.0±1.4	14.0±0.0
Synergy	21.0±1.7	21.0±0.8	24.0±1.4

Sample A: 1.5 mm thick sample; Sample B: 2.5 mm thick sample; Sample C: 3.5 mm thick sample
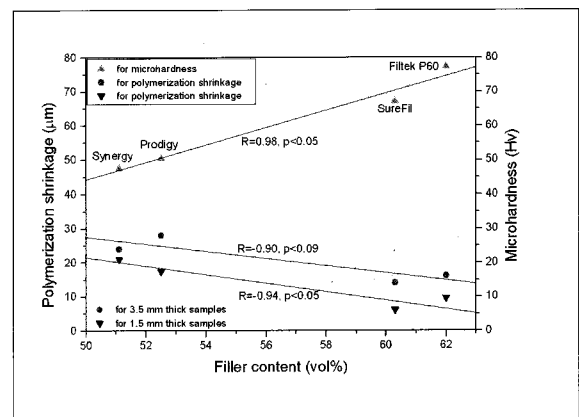
Fig. 3. The correlation between filler content and polymerization and microhardness among the tested samples.

Ⅲ. Results

1. Microhardness test

Table 2 shows the mirohardness of samples for the different stages of thermocycling. Filtek P60 and Synergy showed the highest (77.33±0.93) and lowest (47.55±0.48) values, respectively. After 5000 thermocycles, Filtek P60 and SureFil showed a greater microhardness decrease (14.8% and 10.8%) than Prodigy and Synergy.

2. Polymerization shrinkage measurement

Fig. 1 and 2 show the linear shrinkage profiles of samples during a 300-second period in a different sample thickness. Shrinkage had rapidly increased during the first 40-second period, the time required for light curing, and then it reached a plateau. SureFil and Synergy showed the least and the greatest amount of shrinkage, respectively, in a 1.5 mm sample. Table 3 shows the polymerization shrinkage (μm) of samples, for 300 seconds, during and after polymerization of different thicknesses. In a 1.5 mm sample, SureFil and Synergy showed 6 and 21 μm shrinkage, respectively. Fig. 3 shows the relationships between the filler content (vol%), polymerization shrinkage (μm), and microhardness (Hv). There was an inverse linear correlation between polymerization shrinkage and filler content. The linear correlation (R=0.98) between the microhardness and filler content was found in the tested samples.

Ⅳ. Discussion

Regarding polymerization shrinkage, several factors are known to influence the shrinkage process. The chemistry of the resin matrix is one factor[2,15]. From the composition in Table 1, TEGDMA was observed in the conventional composite resins; Prodigy and Synergy. TEGDMA is a monomer of lower molecular weight compared to Bis-GMA and it is used to dilute high-viscous Bis-GMA in order to assist the dentist. The molecules of a monomer, placed equidistantly by the 'van der Waals' force, are linked with a covalent bonding to form a polymer network. The covalent radius is about one third of the van der Waals's radius. Thus, the magnitude of shrinkage is dependant upon the degree of conversion and the size of the monomer. Adding a monomer of lower weight molecules to lower the viscosity can increase the polymerization shrinkage. The composition of SureFil is urethane modified Bis-GMA. This monomer has a high molecular weight and a lower viscosity compared to Bis-GMA. A lower viscosity implies greater mobility. Polymerization, with less shrinkage, was achieved by the combination of these two characteristics. The UDMA monomer in a Filtek P60 is contained to dilute Bis-GMA instead of TEGDMA. The UDMA monomer has a high molecular weight with a lower viscosity. The Bis-EMA monomer is non-hydroxylated homologues of Bis-GMA. This monomer minimizes water sorption of the resin matrix. This combination of new monomers probably lowered the polymerization shrinkage in a Filtek P60. Polymerization shrinkage is also affected by the filler content. Filtek P60 and SureFil showed similar but a higher filler volume (~62 vol%) than the two other composites (~52 vol%). Since a higher filler volume indicates a lower resin matrix volume, less polymerization shrinkage can be achieved due to a decrease in polymerizable resin volume.

The temperature changes in the oral cavity are routine. The local temperature change in the oral cavity generates a temperature gradient in the local lesion and forms thermal stress. The thermal stress can affect the dental cavity which is filled by dental restorative material. Since the dental restorative material and teeth have different thermal expansion properties, any microdeformations can be formed in the interface. Further thermal stimulation can increase the formed microdefects and induce crack propagation through the bonded interfaces[13,14]. Microgaps can also be formed in the dental cavity due to the polymerization shrinkage of the restorative material.

The microhardness test is an important way of evaluating the degree of polymerization. A positive correlation has generally been established between the microhardness and the inorganic filler content (vol%) of resin composites[6,16]. In our study, the same linear positive correlation (r=0.98, p<0.05) was found among the tested resins. Filtek P60 and SureFil showed approximately 34-60% higher micro-

hardness values than Prodigy and Synergy, even though their filler conent(vol%) were approximately 20% greater than those of Prodigy and Synergy. The highest microhardness value of Filtek P60 may be attributed to the highest filler content (wt% or vol%) and harder filler particles: zirconia/silica. It is interesting to note that during the thermocycling process, only Filtek P60 and Surefil showed a significant decrease in microhardness: 14.8 and 10.8%, respectively, after 5000 thermocycles. Prodigy and Synergy showed negligible microhardness change. The greatest microhardness decrease in Filtek P60 may be due to the high content of silica among the tested materials. Water sorption during the thermocycling process results in swelling of the resin matrix and it introduces tensile stress at the filler-resin interfaces. Also it strains the Si-O-Si bond in the inorganic fillers. The high energy arising from the strained Si-O-Si bonds makes the fillers more susceptible to stress and probably weakens the hardness of the surface. In the case of SureFil, it contains a small amount of silica (1~2 wt%). The weakness of the surface microhardness after the initiation of the thermocycling process is probably attributable to the dissolution of fluoride. SureFil is a fluoride-containing composite resin. During the process, the release of fluoride and ions with surface degradation can be expected[17]. Through the open structure, water sorption and solubility may increase, thus resulting in the decrease of microhardness. An insignificant change of microhardness in Prodigy is probably related to the lower silicon content. The silicon contained in Synergy is hydrophobed. Furthermore, since Bis-EMA minimizes water sorption in the resin matrix, subsequently, there is little change in the level of microhardness in Prodigy and Synergy.

V. Conclusions

Packable composites are the new class of resin composites with a high viscosity and high filler load. Due to these features, packable composites are claimed to undergo less polymerization shrinkage and are a potential substitute for amalgam. Two packable resins (Filtek P60 and SureFil) were used to test their surface microhardness and morphology before and during the thermocycling process. Polymerization

shrinkage was measured during and after the light-curing process. The required results were compared to the results obtained from the two conventional hybrid resins (Prodigy and Synergy).

Each tested sample showed very different microhardness values and among them, packable resin samples showed higher microhardness values than the hybrid resin samples. Filtek P60 and Synergy showed the highest and lowest values. After 5000 thermal cycles, Filtek P60 and SureFil showed the greatest microhardness decrease (14.8% and 10.8%) compared to the microhardness values before the thermocycling process. On the other hand, Prodigy and Synergy showed negligible hardness change compared to their original values. Among the tested resins, a linear correlation was found between microhardness and filler content (vol%). The tested resins showed rapid polymerization shrinkage during the first 40-second period, the time required for light curing, and then reached a plateau. Filtek P60 and SureFil showed less shrinkage than Prodigy and Synergy. There was an inverse correlation between polymerization shrinkage and filler content.

References

1. Venhoven BAM, de Gee AJ, Davidson CL : Polymerization contraction and conversion of light curing Bis-GMA-based methacrylate resins. Biomaterials, 14 : 871-875, 1993.
2. Peutzfeldt A : Resin composites in dentistry: The monomer system. Eur J Oral Sci, 105 : 97-116, 1997.
3. Walls AWG, McCabe JF, Murray JJ : The polymerization contraction of visible-light activated composite resins. J Dent, 16 : 177-181, 1988.
4. St Germain H, Swarz ML, Phillips RW, Moore BK, et al. : properties of microfilled composite resins as influenced by filler content. J Dent Res, 64 : 155-169, 1985.
5. Braem M, Finger WJ, van Doren VE, et al. : Mechanical properties and filler fraction of dental composites. Dent Mater, 5 : 346-349, 1989.
6. Boyer D.B, Chalkley Y, Chan KC : Correlation between strength of bonding to enamel and mechanical properties of dental composites. J Biomed Mater Res, 16 : 775-783, 1982.

7. Chung KH : The relationship between composition and properties of posterior resin composites. J Dent Res, 69 : 852-856, 1990.

8. De Gee AJ, Davidson CL, Smith A : A modified dilatometer for continiuous recording of volumetric polymerization shrinkage of composite restorative materials. J Dent, 9 : 36-42, 1981.

9. Park S.H, Krejci I, Lutz F : Microhardness of resin composite polymerized by plasma arc or conventional visible light curing. Oper Dent, 27 : 30-37, 2002.

10. Aw TC, Nichollas JI : Polymerization shrinkage of densely-filled resin composites. Oper Dent, 26 : 498-504, 2001.

11. Bausch JR, de Lange K, Davidson CL, et al. : Clinical significance of polymerization shrinkage of composite resins. J Prosthet Dent, 48 : 59-67, 1982.

12. Davidson CL, Feilzer AJ : Polymerization shrinkage and polymerization shrinkage stress in poly-mer-based restoratives. J Dent, 25 : 435-440, 1997.

13. Crim GA, Garcia-Godoy F : Microleakage: The effect of storage and cycling duration. J Prosthet Dent, 57 : 574-576, 1987.

14. Torstenson B, Brannstrom M : Contraction gap under composite resin restorations: Effects of hygroscopic expansion and thermal stress. Oper Dent, 13 : 24-31, 1988.

15. Davy KW, Kalachandra S, Pandain MS, et al. : Relationship between composite matrix molecular structure and properties. Biomaterials, 19 : 2007-2014, 1998.

16. Kwon YH, Kwon TY, Ong J, et al. : Light-polymerized compomers: coefficient of thermal expansion and microhardness. J Prosthet Dent, 88 : 396-401, 2002.

17. Combe EC, Douglas WH : The future of dental materials. Dent Update, 25 : 411-417, 1998.

Abstract

A STUDY OF MICROHARDNESS AND POLYMERIZATION SHRINKAGE OF PACKABLE RESINS

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Packable resins have been introduced in the market with high expectations as an alternative to amalgam. They are characterized by a high-filler load and a filler distribution that gives them a different consistency compared with the hybrid resins. The effect of high filler load on the microhardness and polymerization shrinkage of packable resins was tested. Hybrid resins were also tested to compared with the packable resins. As a result, packable resins showed a much greater microhardness value than hybrid resins. All the tested resins have a correlationship with the microhardness and filler content (vol%). The packable resins showed much less polymerization shrinkage than hybrid resins. The filler content and polymerization shrinkage were inversely correlated in the tested resins.

Key words : Packable resin, Microhardness, Polymerization shrinkage