



Low shrinkage light curable nanocomposite for dental restorative material

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Summary Objectives: The aim of this study was to develop a low shrinkage visible light curable nanocomposite dental restorative material without sacrificing the other properties of conventional materials. This nanocomposite was developed by using an epoxy resin 3,4-epoxycyclohexylmethyl-(3,4-epoxy)cyclohexane carboxylate (ERL4221) matrix with 55% wt of 70-100 nm nanosilica fillers through ring-opening polymerization. GPS (γ -glycidoxypropyl trimethoxysilane) was used to modify the surfaces of silica nanoparticles.

Results: The nanocomposite was shown to exhibit low polymerization shrinkage strain, which is only a quarter of currently used methacrylate-based composites. It also exhibited a low thermal expansion coefficient of $49.8 \mu\text{m}/\text{m}^\circ\text{C}$ which is comparable to that of the methacrylate based composites ($51.2 \mu\text{m}/\text{m}^\circ\text{C}$). The strong interfacial interactions between the resin and fillers at nanoscales were demonstrated by an observed high strength and high thermal stability of the nanocomposite. A microhardness of 62KHN and a tensile strength of 47 MPa were reached. A high degree of conversion ($\sim 70\%$) can be obtained after less than 60 s of irradiation upon the nanocomposite. A transmission electron microscope (TEM) study of the nanocomposite showed no aggregation of fillers. Comparable results to the methacrylate based composites were obtained from the one day MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide) cytotoxicity test.

Significance: The developed epoxy resin based nanocomposite demonstrated low shrinkage and high strength and is suitable for dental restorative material applications.

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Introduction

Commercial light curable restorative composites were prepared by mixing organic methacrylate resins with inorganic fillers. Fillers such as SiO_2 , ZrO_2 , Al_2O_3 of micron or submicron particle size are usually used. The organic matrix often comprises of methacrylate resins such as 2,2-bis[4-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane (Bis-GMA) or triethyleneglycoldimethacrylate (TEGDMA). Bis-GMA is the primary organic ingredient in nearly every commercial restorative resin [1,2]. Although the composite based on Bis-GMA has become vital for dental restoration due to its superior aesthetic quality, simple operation technique, and enhanced mechanical strength, there are still problems. The linear shrinkage of microfilled composites ranged from 2 to 3% after curing. Hybrid composites and microhybrid composites shrink from 0.6 to 1.4% [3]. Such shrinkage causes microleakage, a well-known effect of contraction gaps on the interface of resin and tooth. Saliva, fluid, food residue and microorganisms trapped in the gaps lead to decayed teeth and damaged enamel, which is a major problem in current restorative and esthetic dentistry. Therefore, the objective of this study was to provide a material with high mechanical properties and low polymerization shrinkage. It was anticipated that composites with epoxy resin and nanosilica fillers could fulfill these requirements.

Organic-inorganic hybrids have recently emerged as a new class of material which capitalizes on the merits of each species [4-7]. The inorganic phase is nanosized and homogeneously dispersed in the organic matrix to give exceptional strength, hardness and toughness. Organic-inorganic hybrids were used in this study to design and synthesize nano order organic-inorganic composite materials. This research involved two parts: (1) synthesizing the hybrid material and (2) characterizing the hybrid material. The inorganic nanoparticles were chemically modified before they were dispersed in epoxy resin to make a flowable organic-inorganic hybrid material. Photoinitiators and additives were then added to the hybrid resins, which were polymerized by irradiation. It was expected that such nanoparticles would satisfy the criteria of this study for mechanical strength and hardness, while the organic phase delivers the required fracture toughness. In general, resins cured by ring-opening polymerization shrink less as they harden because of the increase in excluded free-volume associated with the ring-opening process. Tilbrook et al. [8] reported that polymerization shrinkage of their epoxy based dental restorative resins improved

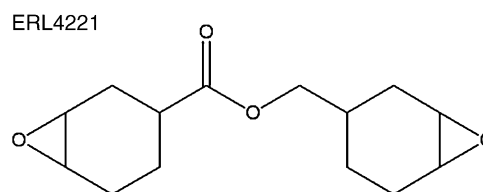


Figure 1 Chemical structure of ERL4221.

2-3% over the traditional methacrylate systems. The good adhesion properties of epoxy resins [9] would be expected to minimize microleakage.

The shrinkage of composites depends on their resin compositions, degree of conversion, filler type and filler concentration. These parameters were studied systematically. For nanocomposite, an improvement in physical properties is expected due to the increased interfacial interactions between resin and fillers [7]. In this study, a visible light curable nanocomposite dental restorative material was developed based on epoxy resin 3,4-epoxycyclohexylmethyl-(3,4-epoxy)cyclohexane carboxylate (ERL4221) and nanosilica fillers. The chemical structure of ERL 4221 is shown in Fig. 1.

Materials and methods

Preparation and curing of nanocomposites

Preparation of light curable epoxy resin (LC-ERL4221)

Light curable epoxy resin (LC-ERL4221) was prepared by mixing 9.52 g of epoxy resin ERL4221 (3,4-epoxycyclohexylmethyl-(3,4-epoxy)cyclohexane carboxylate, Union Carbide), 0.381 g of photoinitiator OPIA ((4-octylphenyl)phenyliodonium hexafluoroantimonate, General Electric) and 0.095 g of photosensitizer CQ (camphorquinone, Sigma). The mixture was stirred for 30 min to ensure homogeneity in a light-tight container.

Preparation of microcomposite (CUS40)

Microcomposite resin CUS40 was prepared by mixing 6.3 g of organic components (ERL4221:OPIA:CQ=1:0.04:0.01 in weight ratio), 4 g of CUS-15 (15 μm SiO_2 powder, CUS-15, Toshiba Ceramic Co.) and 20 g of anhydrous methanol. The mixture was stirred for 30 min in a light-tight container and methanol was then removed under vacuum ($\sim 10^{-2}$ torr) overnight at room temperature with a liquid nitrogen cold trap. The methanol was completely removed using vacuum because no volatile component was detected above boiling temperature of methanol (65 $^\circ\text{C}$) according to thermogravimetric analysis.

Preparation of Z series nanocomposite

The inorganic component of Z series nanocomposites is Silica-A (70-100 nm SiO₂ nanoparticles). Silica-A nanoparticles were obtained by centrifuging ST-ZL (40 wt% 70-100 nm SiO₂, Nissan Chemical Co., Tokyo, Japan) and removing solvent. Silica-A was then dispersed in anhydrous methanol (five times Silica-A in weight) to make a colloidal solution. The concentration of Silica-A in the solution was determined using TGA (thermogravimetric analyzer). Z30 and Z40 were prepared by mixing the required amounts of Silica-A solution and organic components (ERL4221:OPIA:CQ5=1:0.04:0.01), stirring for 30 min in a light-tight container, removing methanol by vacuum ($\sim 10^{-2}$ torr) overnight at room temperature with a liquid nitrogen cold trap.

Preparation of G series nanocomposite

The inorganic component of G series nanocomposites is coupling agent GPS (γ -Glycidoxypropyl trimethoxysilane, A-187, Witco) modified Silica-A. The GPS modified Silica-A was obtained by mixing ST-ZL, GPS (Silica-A/GPS=5/0.5 in weight) and anhydrous methanol (10 times quantity of GPS in weight) by continuous stirring for 24 h at 50 °C, followed by centrifugation of the solution. Then, the GPS modified Silica-A was suspended in anhydrous methanol (5 times Silica-A in weight) to make GPS modified Silica-A solution. The concentration of GPS modified Silica-A in solution was determined by TGA. G30, G40, G50 and G60 were prepared by mixing the required quantities of GPS modified Silica-A solution and the required quantity of organic components (ERL4221:OPIA:CQ5=1:0.04:0.01), keeping them away from light, and stirring for 30 min, removing methanol under vacuum ($\sim 10^{-2}$ torr) overnight at room temperature with a liquid nitrogen cold trap.

Preparation of M series nanocomposite

The inorganic component of M series nanocomposite was a mixture (1:1 by wt.) of coupling agent GPS modified silica nanoparticles of two different sizes (20-30 and 70-100 nm). GPS modified Silica-B solution was obtained by mixing the appropriate quantities of MA-ST-M (40.3 wt%, 20-30 nm SiO₂ in methanol, Nissan Chemical Co., Tokyo, Japan), GPS (with Silica-B:GPS=5:1 by weight), and anhydrous methanol (10 times GPS in weight), and stirring for 24 h at 50 °C. The concentration of Silica-B was determined by TGA. M40 and M50 were prepared by combining GPS modified Silica-A solution, GPS modified Silica-B solution (Silica-A:Silica-B=1:1 by weight)

and organic components (ERL4221:OPIA:CQ5=1:0.04:0.01), stirring for 30 min in a light-tight container, and removing methanol under vacuum ($\sim 10^{-2}$ torr) overnight at room temperature with a liquid nitrogen cold trap.

Preparation of test samples

Nanocomposite samples 15-20 mg from G, Z, and M series were prepared by placing the uncured composite material into a PTFE mold (5 mm in diameter and 2 mm in thickness) and cured with light, either for 1 or 2 min each at the top and bottom sides (a Kerr Optilux 401 curing light was placed 2 mm above the sample for curing).

A Hitachi H-7100 TEM instrument was used to analyze the size and dispersion of nanoparticles in the epoxy resin from an ultrathin TEM sample (~ 60 nm in thickness). The sample was prepared by cutting the cured sample obtained from above by a diamond knife using an ultramicrotome (Leica UCT, Reichert Analytical Instruments) and floated on water, then transferred to a TEM carbon-coated copper grid (200 mesh). Then the sample was examined under TEM instrument.

Nanocomposites characterization

Shrinkage and conversion of nanocomposite after light irradiation

The shrinkage strain of nanocomposite during curing was monitored using a strain gage (Kyowa, KFRP-5-120-C1-6). The backside of the strain gage's sensing circuit was fixed on a piece of silicone rubber (5 cm \times 5 cm \times 7 mm) using cyanoacrylate adhesive. Each uncured nanocomposite sample (5 mm diameter \times 1 mm in thickness) was placed on the sensing circuit and was irradiated by the dental curing light for 1 min. The shrinkage strain was recorded by strain meter (3800, Measurement Group, Inc.) from the beginning of irradiation to the end of shrinkage (about 3 min).

The conversion rate of nanocomposite after dental curing light irradiation was determined by measuring the residual heat of reaction in the sample using differential scanning calorimetry (DSC, TA Instrument TA2920). The following equation shows the calculation. The sample was tested by DSC right after light irradiation for 10, 20 and 60 s, respectively. The DSC test condition was 30-280 °C with 10 °C/min heating rate in a nitrogen atmosphere. No exotherm in the DSC thermogram was observed after the sample was heated to a 280 °C temperature, at

which the maximum conversion was reached after the DSC test.

Conversion

$$= \frac{\text{(Residual heat of reaction obtained from the sample after irradiation)}}{\text{(Heat of reaction obtained from sample without irradiation)}} \times 100\%$$

Thermal properties

The thermal stability and the amount of inorganic composition were measured by thermogravimetric analyzer (TGA, TA instrument TA 2950). The sample was light cured for 2 min and conditioned at 37 °C for one day. The test was performed from 30 to 800 °C at 10 °C/min in air atmosphere. For measuring the coefficient of thermal expansion, a thermal mechanical analyzer (TMA, TA Instrument TA2940) was used from 30 to 250 °C at 10 °C/min in a nitrogen atmosphere. TMA sample sizes for 5 mm × 5 mm × 3 mm were cured under the same condition as TGA samples.

Mechanical properties

Samples for the microhardness test were light cured for 1 min and conditioned at 37 °C for one day. The Knoop hardness test was performed in air with a load of 98.07 mN for 10 s using a Shimatsu, HMV Microhardness Tester. Measurements at five different points were taken for each sample. The average tensile strength of the nanocomposites was evaluated by the diametral compression test. A sample of 6 mm (diameter) × 3 mm (length) was placed on a compression tester (Instron 5566) at a compression rate of 2 mm/min. The samples of the diametral tensile test were cured under the same condition as for the microhardness test samples.

In vitro cytotoxicity test

Samples (6 mm in diameter × 2 mm in length) were cured for 1 min with visible light and conditioned at 37 °C for one day and then sterilized with ethylene oxide (10.5 Psi, 130 °F, 12 h). The cytotoxicity of each sample was evaluated with the MTT test for one day.

Results

Study of material composition and morphology

The chemical compositions of light curable nanocomposite are summarized in Table 1. Cycloaliphatic epoxy resin ERL4221 was used due to its fast curing speed [8].

In the Z series nanocomposites, the maximum content of SiO₂ fillers is 37% and a filler content over 45% makes the composite unable to be cured by light. In this series, a higher concentration of SiO₂ particles without coupling agent GPS has a higher tendency to aggregate into a macrosized cluster that scattered light and reduced curing efficiency. The mismatch refractive index at 632 nm between resin (1.50) [10] and SiO₂ filler (1.45) contributes to light scattering. The more filler present in the composite, the more light scatters. Thus a reduced curing rate is expected with a higher filler concentration.

G series nanocomposites were obtained by using GPS modified SiO₂ fillers. The maximum amount of filler content increased from 37 to 55% compared with the Z series.

Two different sized SiO₂ particles, Silica-A (70-100 nm SiO₂ particle) and Silica-B (20-30 nm SiO₂ particle) were used to prepare the M series nanocomposites to achieve a high filler loading. The amount of GPS for Silica-B was doubled to compensate for its higher surface area. The total inorganic composition for this series of nanocomposites is limited to 49%. The microhardness decreased as the filler content of nanocomposite increased to 52%. Similar defects and cracking lines were formed inside the sample as described in the previous paragraph. The maximum filler loading of 52% is less than expected which may be due to the increased surface area of Silica-B. Thus, there is a balance between filler size and property.

The TEM investigation of nanocomposite G50 is shown in Fig. 2. Nanoparticles were well dispersed in the epoxy resin and no aggregation was observed.

Degree of conversion

Commercial dental restorative materials were usually polymerized in less than 60 s with a degree of conversion from 55 to 75%. Since polymerization is an exothermic reaction, DSC analysis permitted the degree of conversion of nanocomposites to be monitored. The residual heat of polymerization decreased with longer curing time. The relationship between degree of conversion and curing time for

Table 1 Chemical compositions of light curable nanocomposite dental restorative materials.

Series	Sample number	SiO ₂ /GPS (Wt ratio)	SiO ₂ (wt%)	ERL4221 ^a (wt%)	GPS (wt%)	OPIA ^b (wt%)	CQ ^c (wt%)
Blank	LC-ERL4221	None	0	95.24	0	3.81	0.95
Micro	CUS40	CUS-15 ^d / GPS ^e = 5/0	37.27	59.74	0	2.39	0.60
Nano Z	Z30	Silica-A ^f / GPS = 5/0	27.79	68.77	0	2.75	0.69
	Z40	Silica-A / GPS = 5/0	37.27	59.74	0	2.39	0.60
Nano G	G30	Silica-A / GPS = 5/ 0.5	27.19	66.75	2.72	2.67	0.67
	G40	Silica-A / GPS = 5/ 0.5	35.79	57.74	3.58	2.30	0.58
	G50	Silica-A / GPS = 5/ 0.5	43.96	49.18	4.40	1.97	0.49
	G60	Silica-A / GPS = 5/ 0.5	55.64	36.94	5.56	1.48	0.37
Nano M	M40	Silica-A / GPS = 5/0. 5, Silica-B ^g / GPS = 5/1	39.69	53.65	3.96	2.15	0.54
	M50	Silica-A / GPS = 5/ 0.5, Silica-B/ GPS = 5/1	49.34	43.54	4.93	1.74	0.44

^a OPIA (4-octylphenyl)phenyliodonium hexafluoroantimonate: photoinitiator.

^b ERL4221(3,4-epoxycyclohexylmethyl-(3,4-epoxy)cyclohexane carboxylate): epoxy resin.

^c CQ (camphorquinone): photosensitizer.

^d CUS-15: 15 μm SiO₂ powder.

^e GPS (γ-Glycidoxypropyltrimethoxysilane): coupling agent.

^f Silica-A: 70-100 nm SiO₂ obtained from ST-ZL silica colloidal solution.

^g Silica-B: 20~30 nm SiO₂ obtained from MA-ST-M silica colloidal solution.

G60 and M50 is shown in Fig. 3. The results show that M50 cures faster than G60. To achieve 70% conversion, M50 can be cured in less than 20 s, but G60 needs 60 s. Larger filler size (70-100 nm) and higher filler concentration (55.64%) in G60 caused more light scattering from the sample than the smaller filler size (20-30 nm) and lower filler concentration (49.34%) in M50. Thus the curing rate was decreased for G60.

Shrinkage

The strain gage measured shrinkage of G60 was compared with that of commercial methacrylate composite and shown in Fig. 4. The results show that the shrinkage strain of G60 is about a quarter that of the methacrylate based composite. This is the most striking property of our new low shrinkage nanocomposites.

The properties of nanocomposites compared with neat epoxy resin, methacrylate based composite, and microfiller composite are summarized in Table 2. SiO₂ nanoparticles can reduce the thermal expansion coefficient (CTE) of epoxy resin ERL4221 very efficiently. G60 contained higher filler (55.64%) than that of M50 (49.34%), thus exhibiting a lower CTE than M50. The CTE of nanocomposites was comparable to the CTE of methacrylate composite.

Thermal stability of nanocomposites

Using TGA, the thermal stability and composition of inorganic component were measured. Table 3 summarizes the results of TGA. The temperature of 5% weight loss (decomposition temperature of materials) was increased to about 30 °C, as compared with the neat resin LC-ERL4221.

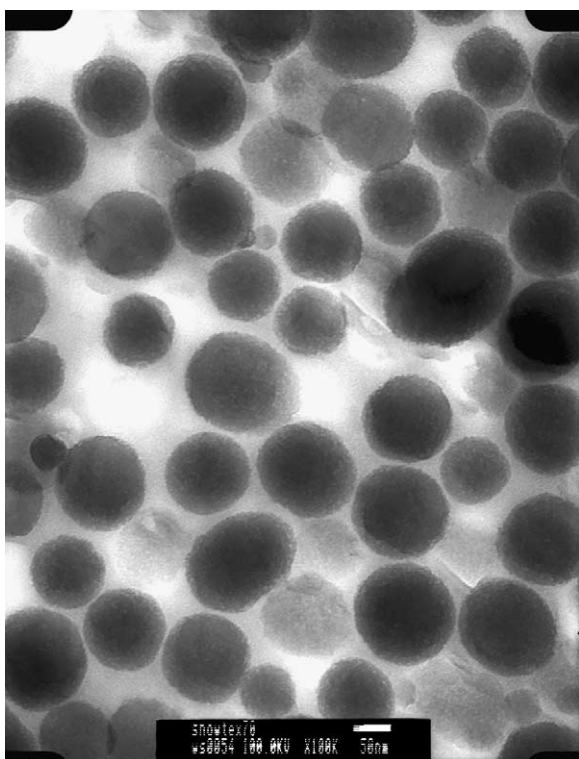


Figure 2 TEM photo of G50 nanocomposite. The nanoparticles are well dispersed in the epoxy resin without aggregation.

The results of TGA in G and M series were similar. As these two series were compared with the neat epoxy resin, an increase of 20-30 °C was observed which was lower than the Z series samples without GPS modification.

Cytotoxicity

One day MTT test results for the cytotoxicity of our nanocomposites were compared and their OD level

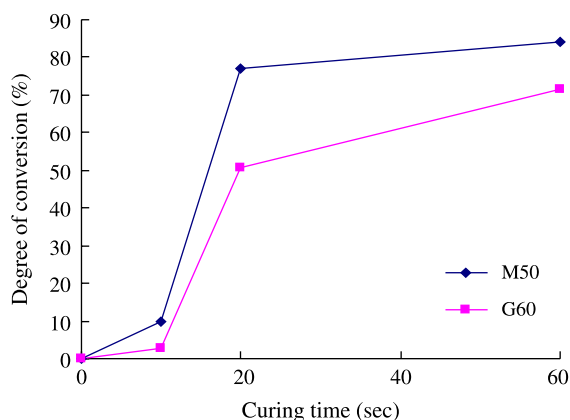


Figure 3 Plot of degree of conversion vs. curing time for nanocomposite G60 and G50. M50 shows a faster curing rate than that of G60.

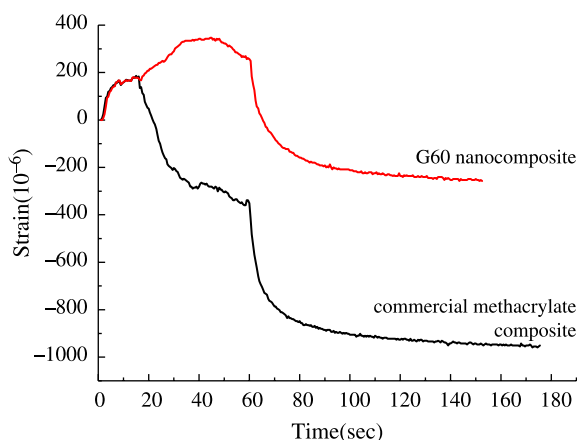


Figure 4 Plot of shrinkage strain vs. time as measured by strain gage. The epoxy nanocomposite exhibits a quarter of the shrinkage strain than that of methacrylate composite.

ranking shown in Fig. 5. The differences between methacrylate composite and nanocomposite are not very significant. Thus, the toxicity of the nanocomposite is comparable to that of commercial methacrylate composite.

Discussion

The photoinitiator used was (4-octylphenyl) phenyliodonium hexafluoroantimonate (OPIA). The OPIA is a cationic type diaryliodonium salts initiator and has a maximum light absorption at 240-250 nm in the UV region. Dental restorative resins require visible light curing because light sources with

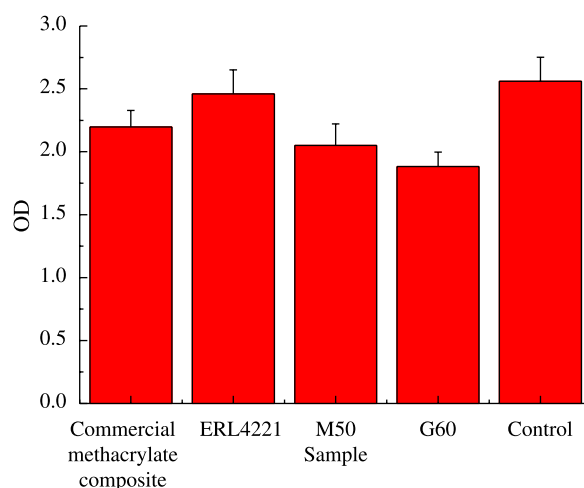


Figure 5 Plot of OD reading vs. different sample for MTT one day test. The results show no significant difference of cytotoxicity between nanocomposites and methacrylate composite.

Table 2 Properties of nanocomposite dental restorative materials.

Sample	CTE ($\mu\text{m}/\text{m } ^\circ\text{C}^{-1}$)	Microhardness (KHN)	Diametral compression test (MPa)
ERL4221 Epoxy resin	123	19	28
M50	56.0	54	42
G60	49.8	65	47
Commercial methacrylate Composite ^a	51.2	62	50

^a Palfique Estelite Paste containing 82% submicron filler used as commercial methacrylate composite.

shorter wavelengths, such as UV or laser, may harm the surrounding tissue. Thus, camphorquinone (CQ) was used as the photosensitizer, which absorbs light in the visible region, then the energy is transferred to OPIA and cations are formed [11]. The cations initiate the polymerization of epoxy resins. Composition without filler (LC-ERL4221) and with microfiller (CUS40) were included in the study for the purpose of comparison.

Colloidal SiO_2 nanoparticle (Silica-A, 70-100 nm) was used as SiO_2 fillers. The outer shell of colloidal particles are surrounded by -OH groups [12]. Negative effects could result from too many nucleophilic -OH groups at high concentrations of SiO_2 , which may react with all of the cationic (electrophile) photoinitiator. Thus, photoinitiated cationic polymerization of the epoxy resin cannot occur [13].

It is desirable to have high filler loading in the nanocomposite that will provide properties of low thermal expansion coefficient and high mechanical strength. The epoxy-functionalized silane coupling agent, GPS (γ -Glycidoxypropyl trimethoxysilane) was used to react with hydroxy groups on the surfaces of silica. Epoxy function on the GPS modified silica filler can also react with the epoxy resin ERL4221 to form a compatible system

between organic phase and inorganic phase. Thus, total loading of inorganic filler can be increased.

It is evident that GPS reacted with the hydroxy group on the surfaces of SiO_2 particles effectively and reduced the reactions with the cationic photoinitiator. When the content of inorganic fillers was increased to 62%, the nanocomposites remain light curable but exhibit low microhardness. This might result from the inadequate concentrations of epoxy to cover all SiO_2 nanoparticles evenly. The inside of these samples had many defects and cracking lines; when a diamond tip of the hardness tester was pressed on these defects and cracking lines, microhardness levels were evidently decreased.

The TEM investigation of nanocomposite G50 showed nanoparticles were well dispersed in the epoxy resin, no aggregation was observed. The result indicates that the surface modification of silica by GPS was very uniform and effective to minimize the surface free energy and to reduce the coagulation of nanoparticles.

The low shrinkage value of nanocomposites is due to the low shrinkage epoxy resin and strong interfacial interactions between resin and nanoparticles. The strong interfacial interactions are investigated in the studies of mechanical properties and thermal properties of the nanocomposites as discussed below.

G60 contained more filler (55.64%) than that of M50 (49.34%), thus exhibiting a lower CTE than M50. The CTE of nanocomposites was comparable to the CTE of methacrylate composite. It is interesting to note that the filler content of methacrylate composite is 82% [14]. From the addition rule, higher CTE for G60 and M50 was expected versus that of methacrylate composite. Such discrepancy may be due to the strong interfacial interactions exhibited between resin and nanoparticles with the large surface area [4]. The same reasons can be used to explain high microhardness and comparable tensile strength of nanocomposites, although they contain less silica filler as compared with commercial methacrylate composite.

Table 3 TGA results of light curable dental restorative composites.

Series	Sample number	Residue (%)	5% Weight loss temp ($^\circ\text{C}$)
Blank	ERL4221	0	295
Micro CUS	CUS40	37.88	331
Nano Z	Z30	27.79	335
	Z40	37.27	340
Nano G	G30	27.19	316
	G40	35.79	321
	G50	43.96	312
	G60	55.64	322
Nano M	M40	39.69	313
	M50	49.34	324

Using TGA, the thermal stability and composition of the inorganic component were measured. The temperature of 5% weight loss (decomposition temperature of materials) was increased to about 30 °C, as compared with the neat resin LC-ERL4221. This results from the presence of inorganic filler, which greatly reduces chemical bond movements of the organic component. The decomposition temperature of Z40 was higher than that of CUS40 (331 °C vs. 340 °C). The results indicate that interfacial interactions were greater in the nanocomposite system (Z40) as compared with the microcomposite system (CUS40). The results of TGA in the G and M series were similar. As these two series were compared with the neat epoxy resin, an increase of 20-30 °C was observed which was lower than the Z series samples without GPS modification. The aliphatic part of GPS and unreacted GPS might play an important role in thermal degradation. Therefore, the amount of GPS needs to be optimized to balance thermal stability with enhanced interfacial interactions.

Conclusions

A visible light curable nanocomposites with low shrinkage, high strength, low coefficient of thermal expansion and low cytotoxicity was developed. The nanocomposite contains various size nanosilica fillers, epoxy resin, cationic photoinitiator and photosensitizer. According to this study, it was found that by using a silane coupling agent with epoxy functional group (GPS) to modify SiO₂ nanoparticles, the dispersion of the nanoparticles was improved, and the loading of nanoparticles was increased. In addition, the GPS strengthens the interfacial interactions between SiO₂ nanoparticles and the organic matrix. Thus, the hardness, thermal expansion coefficient and thermal stability of the nanocomposites are enhanced beyond those of composites obtained from submicron and micron fillers. The ring opening polymerization and strong

interfacial interaction of epoxy based nanocomposite exhibited a low shrinkage strain that was a quarter of the methacrylate based submicro composites.

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References

- [1] Bowen RL, Patent US 3066112, 1962.
- [2] Bowen RL. Compatibility of various materials with oral tissues. I: the components in composites restorations. *J Dent Res* 1962;58:1493-503.
- [3] Craig GC, Powers JM. Restorative Dental Materials Mosby, Inc. 11830 Westline Industrial Drive, St Louis, Missouri 64146 USA 11th Eds. P238-39; 2002.
- [4] Judeinstein P, Sanchez C. Hybrid organic-inorganic materials: a land of multidisciplinary. *J Mater Chem* 1996; 6:511-25.
- [5] Frank CW, Miller RD. *Chem Mater* 2002;14:3676-85.
- [6] Que W. *Chem Phys Lett* 2003;369:354-60.
- [7] Giannelis EP. Polymer layered silicate nanocomposites. *Adv Mater* 1996;8:29-35.
- [8] Tilbrook DA, Clarke RL, Howle NE, Braden M. Photocurable epoxy-polyol matrices for use in dental composites I. *Biomaterials* 2000;21:1743-53.
- [9] Lee H, Neville K. *Handbook of epoxy resins* 1972.
- [10] Su WF and Sun SP. Unpublished data. 2004.
- [11] Pappas SP. *UV curing: science and technology*. 1st ed.: Technology Marketing Corp., Pub. Division; 1978.
- [12] Brinker CJ. *Sol-gel science: the physics and chemistry of sol-gel processing*. 1st ed. New York: Academic Press Inc; 1990.
- [13] Odian G. *Principles of polymerization*. 3rd ed. New York: Wiley; 1991 p. 364.
- [14] Palfique Estelite Instruction for Use; 2001.