

Development of the reinforced acrylic-based hybrid denture composite resin with vinyloligosilsesquioxane(POSS)

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The mainly used polymeric material for the denture is PMMA because of its cost and easiness to handle. So it was widely used material among dentists for past decades. But the acrylic-based denture materials have several common weak points such as shrinkage after curing and lack of strength. In order to solve these problems, we adapted one of hybrid system using acrylic polymer and vinyloligosilsesquioxane(POSS). POSS, which is a well known expandable monomer during polymerization process, may eventually suppress volumetric shrinkage. And the hybrid system makes it possible for the polymer to be stable in various severe conditions. Eight different kinds of samples were designed and synthesized. Each samples were characterized with dynamic mechanical analyser(DMA) to confirm their thermodynamic properties, fractured to analyze the cross-sectional morphology of the samples. And elongation, flexural and impact tests were also executed to evaluate the mechanical properties of the samples. From the results, hybrid composites had well defined crosslinked network structure compared to the widely used denture materials, and the mechanical strength improved without changing any surface condition as increment with POSS ratio in hybrid system. Fractured morphology showed homogeneous surfaces in spite of mutli component system, therefore we can conclude that the adoption of the POSS brought the reinforcement of the denture resin.

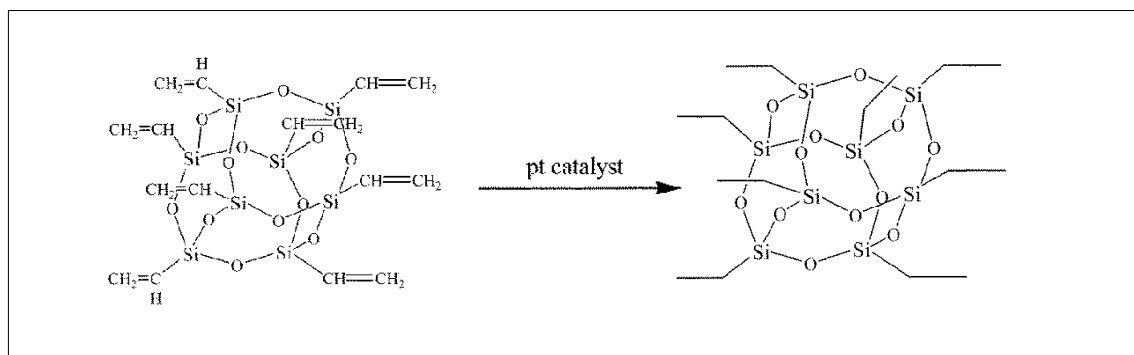
Key Words :

Denture resin, PMMA, Vinyloligosilsesquioxane(POSS), Hybrid system, Thermodynamic property, Mechanical property, Shrinkage suppression

The first rise of the artificial denture materials occurred 70 years ago. Although acrylic polymers were widely adapted for most of denture materials, there had been enormous approach to improve the resin properties by mechanically and thermally in addition to enhance strength and reduce its weight.¹⁴ But there still exist several weak points in polymeric materials compared with ceramics and metallic materials. One of those is volumetric shrinkage after curing process undergoing high temperature and pressure. For example, volumetric shrinkage occurred in the range

of 6~20 % after curing (in various commercialized resins) because of unreacted monomers and thermal recovery of expanded polymeric materials after annealing. This shrinkage would directly introduce unfitting of denture in oral cavity and also cause patient's pain.

To overcome above weak points, we tried to design and synthesized novel organic-inorganic hybrid denture materials (hybrid composite) based acrylic polymeric materials and monomeric vinyloligosilsesquioxane (Scheme 1). Obtained hybrid composite have all the advantages of



Scheme 1. The basic scheme of the PMMA/MMA copolymerization with POSS.

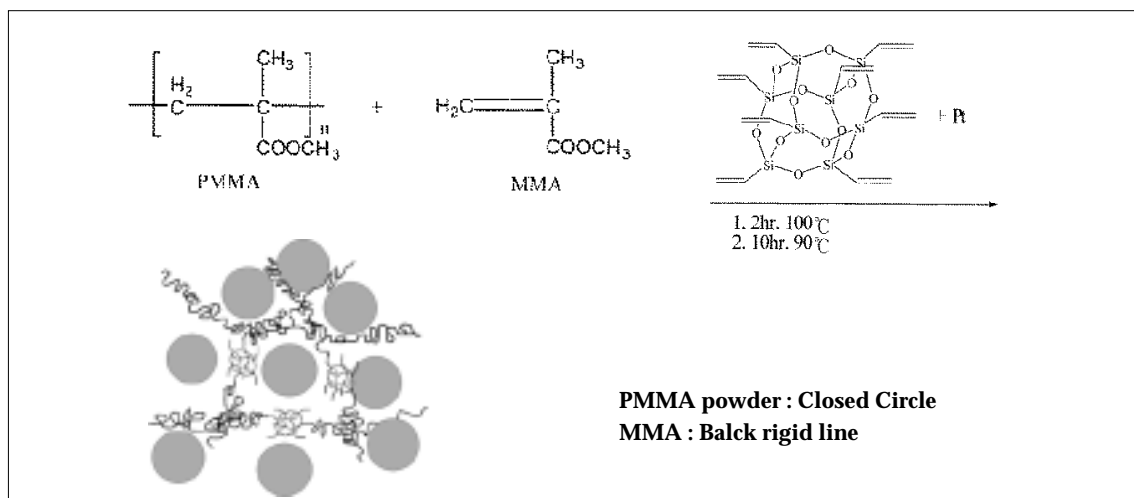


Fig. 1. The basic chemical reactions in copolymerization of the PMMA/MMA with POSS and the structure of obtained network. PMMA powder: Closed Circle MMA network: Black rigid line

polymeric materials and also keep the superior characteristics of inorganic materials (originated from silicone derivatives) (Fig. 1).⁵

Vinyloligosilsesquioxane (POSS), one of expandable monomers, have 8 vinyl functional groups in its own molecular structure, so in polymerization those double bonds in vinyl groups act as a crosslinker to make network structure between PMMA and MMA matrices. As the results, POSS containing polymer shows very elastic and toughened characteristics in relation to the increment of Si-O linkage which may absorb external stress.⁶ Additionally, high thermal stability and anti-abrasion ability are also expectable in such anti-shrinkable POSS composite because of its network structure.

In this article, we tried to develop the PMMA-POSS hybrid composite system and characterize that how POSS functions in acrylic polymer matrix in order to build up complete denture material compared with commercial acrylic based denture resin.

MATERIAL AND METHODS

Materials

The Paladent[®] 20 (Heraeus Kulzer, Germany) was purchased and used as base denture resin. The 1,3,5,7,9,11,13,15-octavinylpentacyclooctasiloxane (POSS; Aldrich Chemical, US), and platinum-divinyl tetramethyldisiloxane complex (Gelest, US) were purchased and used without further purification. Other solvents (THF and Methanol, Aldrich Chemical, US) were purchased and used without further purification.

Experiments

Preparation of denture sample for control

The polymer (Paladent, PMMA particle) and monomer (MMA, liquid) were mixed under the ratio of 3.3 : 1 (vol %, exactly 10g : 4ml) using vacuum mixer and put into the mold (SKD-11 ; Fe 86 %, Cr 11 %, C 1.4 %, Mo 0.8 %, others 0.7 % ; 95 ×

95 × 5 mm) carefully preventing air bubble formation. Then the mold was placed on the hot press and pressed under 5 metric ton at 100 °C for 2 hours. The mold was annealed for 2 hours additionally and was opened after air cooling, the sample was separated from the mold.

Preparation of original reinforced denture sample

POSS was dissolved in MMA monomer before mixing with polymer. Only 1.44 % of POSS dissolved in MMA monomer. In order to increase the solving fraction, small amount of THF was added into the MMA monomer (MMA:THF 1.7 : 1 vol%). In this way, 3.9 % of POSS-MMA solution could be prepared. And the Pt catalyst was added to increase the reactivity of monomers in polymer network.⁶ Eight kinds of different samples were prepared as shown in Table 1 and they were all compared with each other to find out which sample would show best reinforcing properties.

Physical Property Tests

All the samples were placed in the vial and 30 ml of acetone was poured into the vial for the investigation of swelling behaviors. Then the samples were kept in the room temperature for 300 hours.

The cured samples were cut (2 cm × 5 cm × 0.5 cm) with diamond cutter for the surface and inner morphology investigation. The samples surfaces were carefully observed with optical microscopy and the cross sectional area with SEM to investigate the inner pores and roughness.

The Dynamic Mechanical Analysis (DMA : TA instrument, USA) measurements were performed to characterize the thermodynamic properties of the samples.

The flexural, elongational, and impact strengths were all measured according to the standard methods. The flexural and elongational tests

were executed using Instron. The impact test was done with Dynatub®(POE 2000, Instron, USA). The speed of elongation crosshead and flexural crosshead was 10 mm/min and 7.5 mm/min respectively.⁷ The measurements were repeated 4 times for each samples. Additionally, the modulus of each samples were recorded.

RESULTS

Synthesis of the samples

The samples had been synthesized under accurate temperature and pressure control to minimize structural defects occurring in polymerization process. If the temperature of the mold rose over 150 °C, the materials showed too much elasticity. If the temperature was not high enough, there were too much bubbles and the polymerization finished before complete conversion of monomer, this would eventually brought lower mechanical strength of the samples. After curing, all the samples should be annealed before opening mold to minimize the samples strain or rapid shrinking.

The outlook morphology of the samples

The cured sample surfaces were extremely clean and bubbleless all over the surfaces. The cross sectional area of the samples were also homogeneous. The adoption of the THF did not alter the surface condition by optical microscopy observation. But it is thought that the evaporation of THF at lower temperature makes it possible for the resin to form very small vacant spaces inside the cured sample, therefore we can not deny the residence of THF as residue in cured samples.

There was distinguished differences between PMMA/MMA resin for control and POSS-adopted sample. As shown in Figure 2, we can observed that PMMA particles kept their own shapes in fractural surfaces because of insufficient forming of network structures, which led to interfacial vacant volume between PMMA particles and polymerized MMA matrix. But in POSS-adopted samples, original PMMA particle shapes were no longer observed, this means that there was newly formed network structure by way of crosslinking the MMA and vinyl groups in POSS. So it is possible to conclude that the POSS do affect the outlook and inner morphology of denture resin.

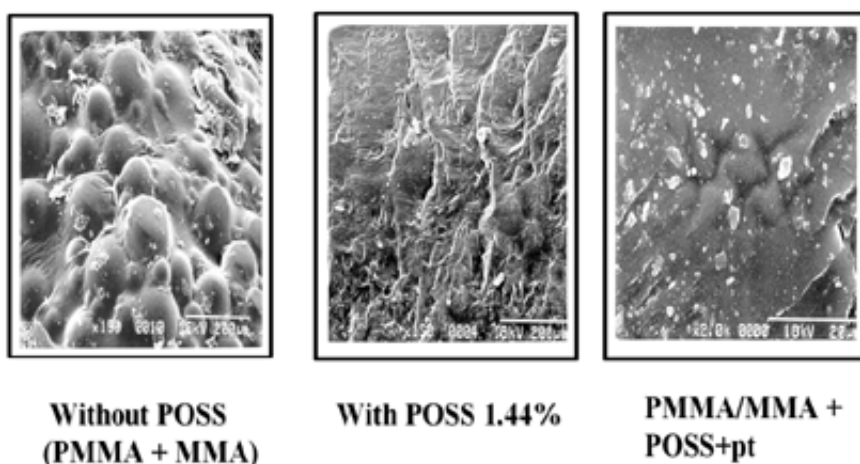


Fig. 2. Surface morphology of PMMA/MMA and POSS samples.

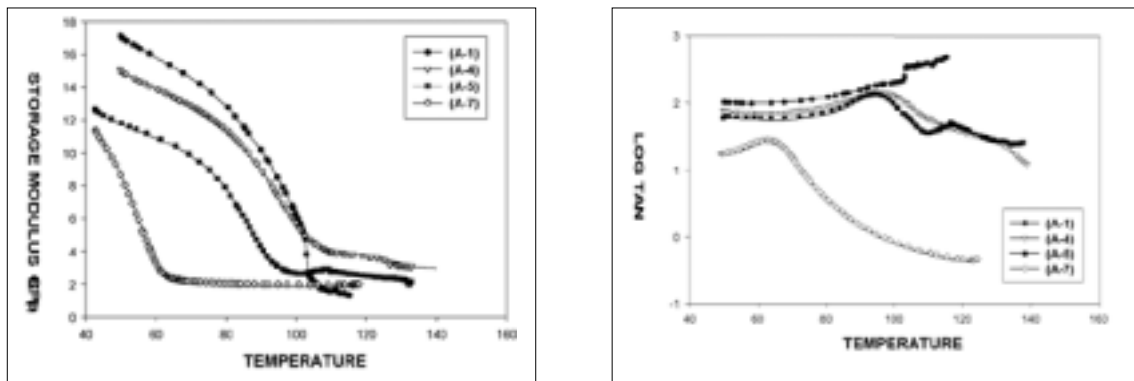


Fig. 3. The DMA behavior of the samples: 1) gain modulus, 2) tan

The thermodynamic properties of the samples

As seen in Figure 3, respective samples showed typical but individual thermodynamic characteristics. In case of control sample, PMMA/MMA did not show crosslinking behavior and we could not obtain traditional DMA curve of well known PMMA samples (A-1 curve in Figure 3 (b)). But in other samples, in which POSS is added, crosslinking behavior is revealed out and we could obtain such a original DMA curves of PMMA. Additional crosslinking verifications were that E' value above T_g were observed in high level in comparison with uncrosslinked PMMA (A-4 and A-1 curves in Figure 2 (a)). From the DMA results, T_g of one of POSS samples is shown at around 105 °C, which is very typical temperature for PMMA.⁸ Additionally, in case of the usage of THF in order to increase POSS portion in MMA solution (A-7), E' behavior showed very different profile compared A-3 and A-4 because of insufficient linkage between PMMA and newly formed MMA network including POSS.

Swelling behaviors

No samples were soluble in acetone and methyl alcohol which were good solvents for PMMA and MMA respectively. They swelled instead

in above solvents, but the swelling behavior was quite different according to the sample compositions. PMMA/MMA sample (A-1, A-2) swelled, but these samples swelled while the surface peeling off and the swelling occurred through the layer. Data in Table II were the another proofs that these A-1 and A-2 samples did not show crosslinking behaviors shown in previously mentioned DMA data. For the cases of POSS samples (A-4 to A-8), the surfaces also swelled but did not separate by inlayers. This indicated that such sample did crosslink inside of the samples.

The morphology of the fractured samples

From the surface morphology data in Figure 4, the differences between PMMA/MMA (A-1, A-2) and POSS-adopted samples (A-2 to A-8) were that PMMA/MMA materials were more rugged. This result means that fracture was not occurred along the interfacial area between PMMA particle and newly formed PMMA matrix by way of MMA polymerization with POSS. Generally, in case of reinforced denture resins, fractural pathway was obtained crossing over the PMMA particles.⁹ In three-dimensionally crosslinked materials, like POSS samples, interfacial force between PMMA particles and MMA matrices was enhanced by POSS and Pt catalyst. Then fracture was

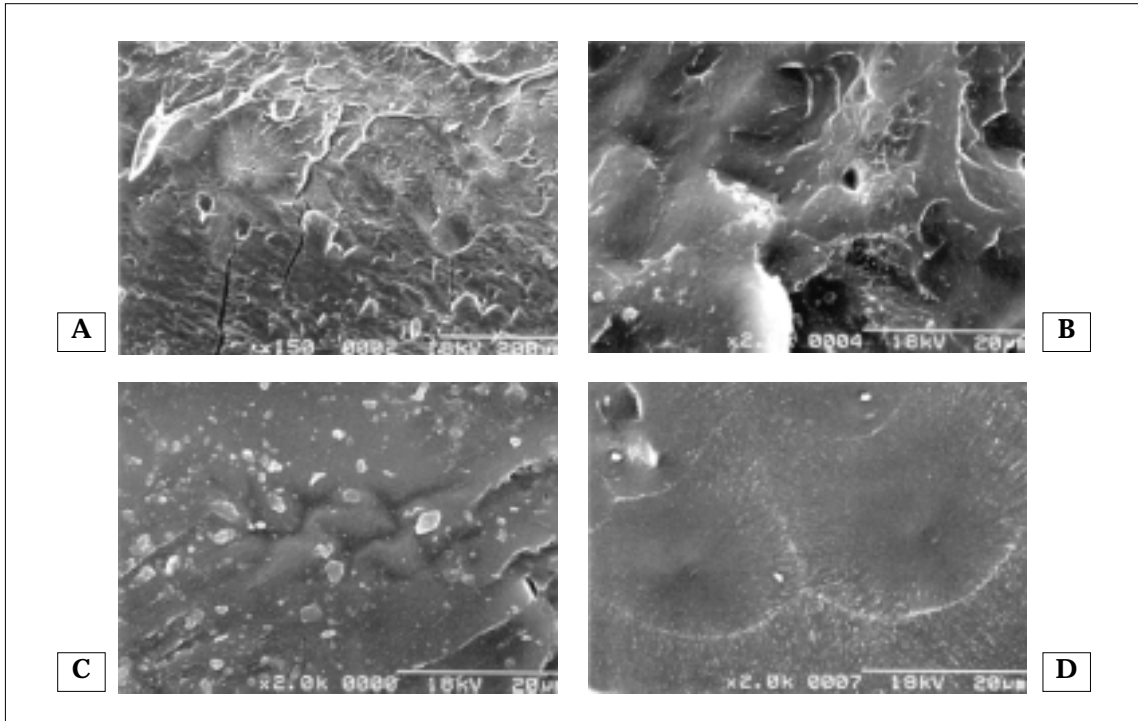


Fig. 4. The fractured surface of the samples viewed with SEM. a) PMMA/MMA, b) PMMA/MMA+POSS, c) PMMA/MMA+POSS+pt, d) PMMA/MMA+POSS+pt in THF

Table I. Sample specifications in this study

Classification	Composition	Curing time
A-1	PMMA/MMA	2hrs
A-2	PMMA/MMA	10hrs
A-3	PMMA/MMA+POSS	2hrs
A-4	PMMA/MMA+POSS+pt	2hrs
A-5	PMMA/MMA+POSS+pt	10hrs
A-6	PMMA/MMA(1)+THF(1)/POSS+pt	2hrs
A-7	PMMA/MMA(1)+THF(2)/POSS+pt	2hrs
A-8	PMMA/MMA(1)+THF(2)/POSS+pt	10hrs

occurred in the part of weaken PMMA particles and we could observe very smooth fractural surface.

The elongational test results

All of samples showed very rigid properties, so they did not show yield point. From the strain modulus data, elongation strength was increased

with introduction of POSS for additional crosslinker and pt for polymerization catalyst (Fig. 5). Especially modulus data of A-3 and A-4 were superior to that of A-1 and A-7. This means that POSS caused supplemental chemical linkage with MMA vinyl groups and finally reinforced crosslinking network structure by the aid of pt catalyst.

The flexural test results

Flexural modulus values of all samples were shown in Figure 6. In case of POSS-adopted samples(A-3 to A-8) had high modulus values comopared with PMMA/MMA samples(A-1, A-2) and this tendency was also shown in samples which were polymerized with pt catalyst. This means that pt actuated all of vinyl groups in POSS to react with MMA vinyl groups in good connection, and these results were deeply relat-

Table II . Swelling data of samples

Classification	Original Density (Weight)	Density after 24 hours in acetone	After 24 hours in acetone (Weight/increment)	Increment in volume	
A-1	1.0696g/cm ³ (0.584g)	0.6238g/cm ³	2.861g/389.90%	740%	Partly peeled
A-2	1.0480g/cm ³ (0.464g)	0.9312g/cm ³	2.244g/383.62%	443.59%	
A-3	1.1525g/cm ³ (0.401g)	0.9888g/cm ³	1.495g/272.82%	334.83%	
A-4	1.0995g/cm ³ (0.442g)	0.9457g/cm ³	1.887g/326.92%	396.81%	
A-5	1.1901g/cm ³ (0.432g)	0.8441g/cm ³	2.231g/416.44%	628.14%	
A-6	N.A.	-	-	-	-
A-7	1.1324g/cm ³ (0.763g)	0.9025g/cm ³	2.702g/254.13%	344.32%	Partly cracked Err.
A-8	1.1215g/cm ³ (0.609g)	0.4977g/cm ³	3.460g/470.02%	1184.46%	

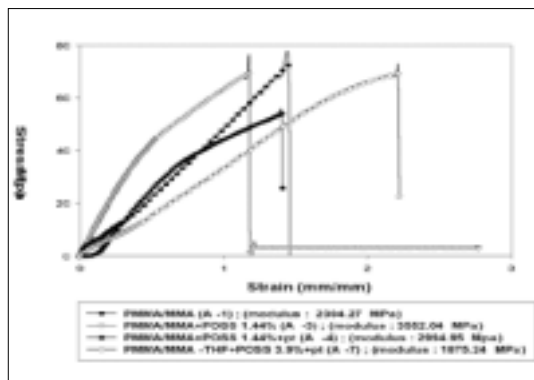


Fig. 5. The elongation test result of the samples.

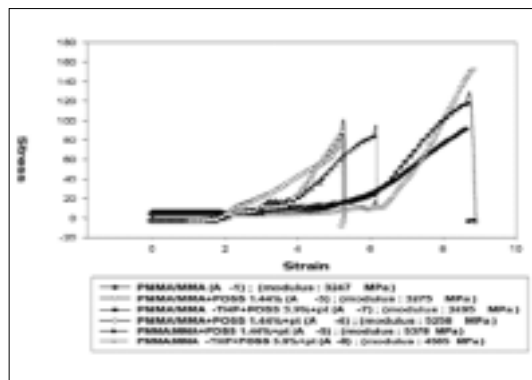


Fig. 6. The flexural test results of the samples.

Table III . Impact test data

Classification	Strength (kg-mm/mm)	Standard Deviation
A-1	1.487	0.540
A-2	1.513	0.265
A-3	1.910	0.211
A-4	2.270	0.618
A-5	1.990	0.467
A-6	-	-
A-7	1.927	0.117
A-8	1.747	0.160

ed to the well developed network structure surrounded PMMA particles.^{10,11} But in spite of large portion of POSS in A-7, flexural modulus had lower level than A4 and A-1 samples. This was explained that the usage of THF in order to increase POSS portion in MMA solution led

to insufficient linkage between PMMA and newly formed MMA network including POSS.

The impact test results

As shown in Table III , impact strength of A-4 was greater than that of PMMA/MMA samples(A-1, A-2). And this tendency was same compared with large POSS portion samples(A-7, A-8). According to the flexible Si-O bonds in POSS, exposed impact stress was absorbed to the POSS fraction which was densely connected to MMA vinyl groups by way of crosslinking reactions. But impact strength of A-7 and A-8 were decreased with the increment of POSS contents. This was the reason that THF, which was adapted to increase POSS solubility in MMA solution, caused loosening the POSS composite structure by vaporization in

polymerization process.

DISCUSSION

POSS, which is one of non-shrinkable monomers containing cage structure consisted of Si-O bonds,¹² was used for reinforcing component in this study for its structural characteristics owing to flexible Si-O linkage. So our strategy was to attempt the modification of mechanical properties of denture matrix using above mentioned advantages of POSS. POSS can be hybridized with copolymerization of various monomers, like as styryl, acrylics, polyamides and LC polymers.¹³ As expected, POSS had a original role as anchoring part in hybrid composite and shock absorption part to external stress owing to its unique cage structure. Because of non-solubility of cured POSS samples in any other organic solvents, we could not detect chemical linkage between POSS and MMA directly, but it was clear that the cured matrix was builded up through vinyl groups opening reaction on the basis of DMA data.

In case of POSS/pt sample, enhanced mechanical strength was observed compared without pt sample. This catalyst acted as a trigger for opening vinyl groups in POSS, then all of 8 vinyl groups participated in connection reaction with MMA vinyl groups, finally build up a 3-dimensionally crosslinked network structure. Therefore we can get superior denture materials using acrylic resin.

In this study, we focused reinforcing effect of POSS owing to its structure and our system showed well established properties in mechanical properties compared PMMA/MMA system or fiber reinforced system.⁴ Additionally we are also on going volumetric anti-shrinkage effect in curing process using POSS in same system.

CONCLUSIONS

1. The cured samples all showed very smooth and clean surfaces.

2. The addition of POSS do not change the outlook morphology, but fractured surface was completely different. POSS reacted with MMA and formed dense network structure. When fractured, fracture was formed across the PMMA particle, the smoothness of the fractured surfaces were observed, meaning that the interactions between PMMA and newly build up MMA matrix were very strong.
3. Flexural and impact test result showed that as POSS is added, mechanical strength increases, but not as so when more POSS is added via THF.
4. The longer curing time made it possible for POSS to polymerize make eventually make harder polymer sheets, but this is not the key factor for reinforcing denture materials. Instead, addition of polymerization catalyst(pt) was more effective for toughening.

This study was supported by Korea Ministry of Health and Welfare Foundation Grant (HMP-99-E-10-0003).

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