

Preparation and Physical Properties of Photopolymer/SiO₂ Nanocomposite for Rapid Prototyping System

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ABSTRACT: A photopolymer material was applied in liquid rapid prototyping (RP) machine. The prototype fabricated from photopolymer was difficult for storage due to volumetric shrinkage and deformation during curing. The prototype fabricated from photopolymer suffers from the volumetric shrinkage during curing and the continuing deformation for a creeping period after curing. Therefore, we used nano-SiO₂ as a major additive to modify the physical properties of photopolymer. We also added appropriate dispersant to make nanoparticles distribute uniformly in order to reduce the

phase separation in composite material. The experimental results showed that photopolymer/SiO₂ nanocomposite can improve tensile strength and hardness by about 50% and offers better dimensional stability. Photopolymer/SiO₂ nanocomposite can also increase the degradation temperature and shorten manufacturing time for RP processing. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3529–3534, 2008

Key words: rapid prototyping; photopolymer; nanocomposite; SiO₂; dispersant

INTRODUCTION

In general, there were solid, powdery, and liquid materials available for rapid prototyping (RP). The most often used material in liquid RP system was photopolymer, which was cured through optical radiation in points, lines, and areas to fabricate the prototype. Currently, liquid RP machines include SLA (stereolithography apparatus, manufactured by 3D Systems, Rock Hill, SC), SGC (solid ground curing systems, manufactured by Cubital, Industrial Zone North, Raanana, Israel), SCS (solid creation system, manufactured by D-MEC, Tokyo, Japan), SOUP (solid object ultraviolet-laser printer, manufactured by CMET, Tokyo, Japan), and SLP (solid laser-diode plotter, manufactured by Denken Engineering, Oita, Japan).¹

The components of photopolymer included reactive oligomer, reactive monomer, photoinitiator, and other special additives, etc. The prototype fabricated from photopolymer was difficult for storage due to volumetric shrinkage and deformation during curing. As the prototype was made of polymer material, the prototype had inherently poor mechanical strength and thermal stability. Therefore, inorganic fillers, such as glass fiber and carbon black, etc. were often added to improve the properties of polymer materials.

In 1999, Cheah et al. added short glass fiber in stereolithography process of photopolymer, and

studied the mechanical property of prototypes. The tensile strength was improved as demonstrated in the experiment.² Zak et al. proved that, when adding short glass fiber of 20% volume ratio into photopolymer, the modulus of prototype increased about 60% than that of pure photopolymer prototype.³

The reinforcement effect of polymer composite materials often depends upon the dispersion effect of inorganic filler in polymer matrix. Filler of a smaller size had a better dispersion effect, reinforcement effect, and a higher interfacial force in composite materials.⁴ Traditional composite materials not only employed lots of additives to improve the reinforcement effect, but also led to higher viscosity. For this reason, there was a demand on nanocomposite materials. The dispersed phase of nanocomposite materials was almost inorganic materials, and the particle size of nanocomposite was between 1 and 100 nm. Because the interfacial area between dispersed phase and continuous phase in nanocomposite materials was much larger than traditional composite materials, the amount of nanoparticles as reinforcing fillers can be significantly reduced. For example, nanocomposite materials based on photopolymer can be mixed with some nanoreinforcing fillers such as clay (silicate nanoparticles), nano-TiO₂, nano-SiO₂, nano-CaCO₃, nano-CB (carbon black). The major function of these fillers was to improve the strength of matrix and shorten the curing reaction time.^{4–6} However, the relevant researches were all limited on coating materials.

In the literature of rapid prototyping technology, the physical properties of photopolymer/nanocomposite have not yet been discussed. The physical properties of photopolymer were modified with the

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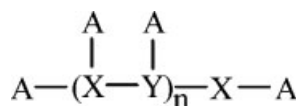
additive nano-SiO₂. Dispersant was mixed within nanocomposite materials to uniformly distribute the nanoparticles. In this article, we observed the phase distribution by scanning electron microscope (SEM), and explored the curing behavior by rigid-body pendulum rheometer (RPT). Moreover, we applied thermogravimetric analyzer (TGA) to test the thermal stability. Through test and analysis of curing thickness, tensile strength, hardness, dimensional stability, and volumetric shrinkage, improvements of the mechanical property and formability with rapid prototyping technology of the photopolymer/SiO₂ nanocomposite were verified.

EXPERIMENTS

This section describes reagents used, the preparation steps as well as experimental items.

Reagents

1. Tetrafunctional polyester acrylate (TPA)
Supplier: Henkel
Type: photomer 5430
Structural formula:



X: polyalcohol, Y: polybasic acid, A: acrylate

2. 1,6-Hexanediol diacrylate (HDDA)
Supplier: Henkel
Type: photomer 4017
Structural formula:



3. Photoinitiator
Supplier: Ciba
Type: IRGACURE 784
Molecular formula: C₂₉H₁₇TiF₃N₂
4. Dispersant
Supplier: Degussa
Type: TEGO Dispers 680UV
5. nano-SiO₂
Supplier: Degussa
Type: Aerosil 200
Size of particle: 12 nm

Material preparation steps

At first, the dispersant was filled into TPA, and stirred for 30 min by a 1000-rpm stirrer. Second, nano-SiO₂ was added into a resin containing dispersant, and stirred for 24 h at 1000 rpm under room temperature. Then, HDDA and photoinitiator were

TABLE I
Formulations of Photopolymer/SiO₂ Nanocomposites

Sample	TPA/ HDDA (phr)	Photoinitiator (phr)	nano-SiO ₂ (phr)	Dispersant (phr)
S ₀₀ D ₀₀₀	100	1.5	–	–
S ₀₅ D ₀₀₀	100	1.5	0.5	–
S ₀₅ D ₀₀₅	100	1.5	0.5	0.5
S ₀₅ D ₀₂₅	100	1.5	0.5	2.5
S ₀₅ D ₀₅₀	100	1.5	0.5	5.0
S ₀₅ D ₀₇₅	100	1.5	0.5	7.5
S ₀₅ D ₁₀₀	100	1.5	0.5	10.0
S ₁₀ D ₀₀₀	100	1.5	1.0	–
S ₁₀ D ₀₁₀	100	1.5	1.0	1.0
S ₁₀ D ₀₅₀	100	1.5	1.0	5.0
S ₁₀ D ₁₀₀	100	1.5	1.0	10.0
S ₁₀ D ₁₅₀	100	1.5	1.0	15.0
S ₁₀ D ₂₀₀	100	1.5	1.0	20.0

added to the mixing resin, and stirred for 30 min at 1000 rpm. The recipe obtained from the resin in the previously specified manner is listed in Table I. The unit “phr” means the parts per hundred parts of TPA/HDDA resin.

Scanning electron microscopy

To know the dispersion of nano-SiO₂ in the mixing resin, a scanning electron microscope, Cambridge S-360, was used to observe the surface feature and phase distribution of gold-plated test piece with a 1000× magnification factor.

Test of rapid-body pendulum rheometer^{7,8}

A rigid-body pendulum rheometer, model RPT-alpha 100, manufactured by Tohoku Electronic Industrial (Tohoku, Japan) was used in this experiment, and its typical curing curve was shown in Figure 1. The analytical principle was explained below: chemical crosslinking occurs at point 2 in the curve, and the oscillation period starts to decline; the first point of inflection is the gel point and the corresponding time means the gel time; slope of 3 → 4 represents the crosslinking speed of materials, namely, the reaction speed; the curve becomes gentle at point 6, indicating that the reaction has reached a balanced state; the last point of inflection is curing point and the corresponding time means the curing time; the curing reaction time is the interval between gel point and curing point. In accordance with ISO1522,⁹ a knife-edge pendulum (serial. no. RBE-130; frame type: FRB-200) was applied for this experiment.

Analysis of TGA

TGA2950 thermogravimetric analyzer (developed by TA Instrument, New Castle, DE) was applied to re-

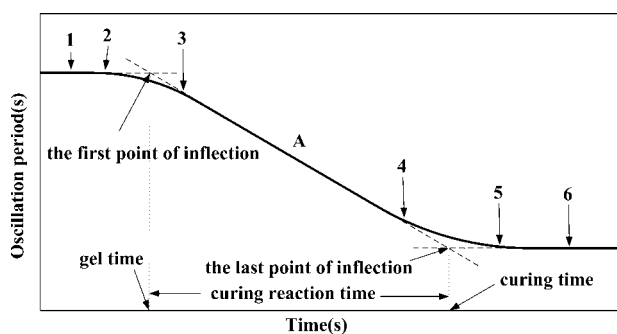


Figure 1 The typical curing curve of RPT.^{7,8}

cord the change of weight and temperature with N₂ and temperature rise to 700°C at 20°C/min.

Mechanical properties

The tensile test piece was designed as per ASTM D638-95,¹⁰ with a spacing of 65 mm and tensile speed of 30 mm/min. Tensile strength experiment was conducted using a universal tensile tester (UMT), JIA701, to measure the tensile strength. The mean value of five measurements was taken.

In accordance with ASTM D2240,¹¹ Type A durometer with 1 kg deadweight was applied for hardness test. "HA" means hardness reading on Type A durometer. The specimens were molded with dimension of 2 cm × 2 cm × 0.6 cm. The data represented the average values of five test specimens.

In accordance with ASTM D2566,¹² pycnometer and densitometer were used to measure separately density ρ_1 and ρ_2 before and after curing reaction. The volumetric change was obtained from density

conversion, with volumetric shrinkage S calculated from eq. (1).

$$S = \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) / \frac{1}{\rho_1} = \left(1 - \frac{\rho_1}{\rho_2} \right) \times 100\% \quad (1)$$

The basis properties for RP system

All current RP processes use layered approach to build parts. We called the thickness of each layer as curing thickness in RP processes. In curing thickness experiment, we used a projector to generate photomask via a blue lens filter. The photopolymer was placed into resin tank, where the resin was exposed to blue light with irradiation periods of 10, 20, 30...80 s. Then, a micrometer was used to measure and record the thickness of the exposed resin. The RP machine with a photomask of 2 × 2 cm² was applied for this experiment.

In accordance with ASTM D1204,¹³ rectangular column prototypes of fixed size were fabricated by the RP machine with samples of S₀₀D₀₀₀, S₀₅D₀₀₀, S₁₀D₀₀₀. Three days after these prototypes were placed into thermostatic chamber, we measured the size of samples with a micrometer and calculated the dimensional shrinkage.

RESULTS AND DISCUSSIONS

Composite morphology

Samples with an additive of nano-SiO₂ 1 phr were investigated. Figure 2(a) depicted a SEM photo of S₁₀D₀₀₀ and Figure 2(b) depicted a SEM photo of S₁₀D₂₀₀. The magnification photos from SEM showed

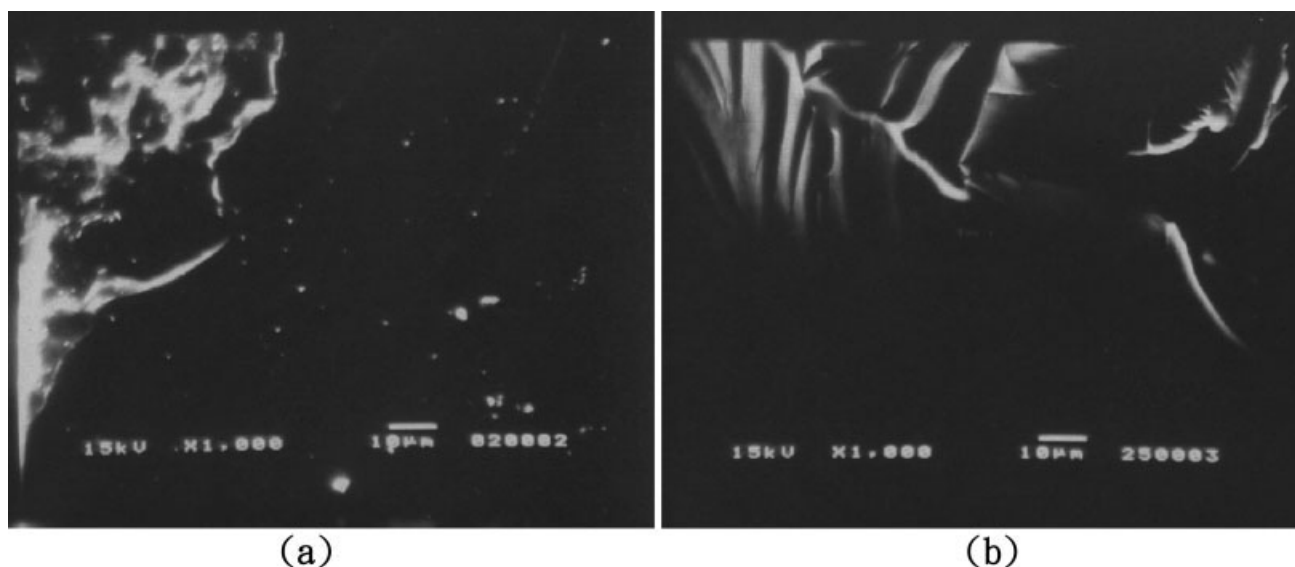


Figure 2 (a) SEM photo of S₁₀D₀₀₀, (b) SEM photo of S₁₀D₂₀₀.

that the dispersant enabled nanopowder to be distributed uniformly in the resin without aggregation.

Analysis of photocuring behavior

We can observe the photocuring behavior of photopolymer through a rapid-body pendulum rheometer during curing. The inflection points and the curing times were obtained from RPT instrument. The results showed that the curing time of $S_{00}D_{000}$ was 110 s and the slope between gel point and curing point for curing was about 2.5. In Figure 3, the curing time of $S_{05}D_{000}$ was 95 s, which is 15 s faster than $S_{00}D_{000}$. It showed that curing reaction time was shortened and reaction speed became faster for the sample with nano- SiO_2 . By further incorporating dispersant into the composite resin, the curing reaction time can be reduced to 90 s, as shown in the curve of $S_{05}D_{005}$. In Figure 4, the curing reaction time was also shorter after adding nano- SiO_2 1phr and dispersant into the sample $S_{00}D_{000}$. In other words, the manufacturing time of prototypes were shortened during RP processing.

Analysis of thermal property

The degradation temperature and thermal stability of polymer was investigated with analysis of TGA. These properties are critical to the storage of prototypes. Figure 5 depicted TGA test results, wherein the initial degradation temperature of $S_{00}D_{000}$ was $\sim 268^\circ\text{C}$, and complete degradation temperature was $\sim 489^\circ\text{C}$. The initial degradation temperature of $S_{05}D_{000}$ was $\sim 335^\circ\text{C}$, and complete degradation temperature was $\sim 507^\circ\text{C}$. As seen from the curves of $S_{00}D_{000}$ and $S_{05}D_{000}$, additive of nano- SiO_2 can increase the degradation temperature of TPA/HDDA resin. The initial degradation temperature of

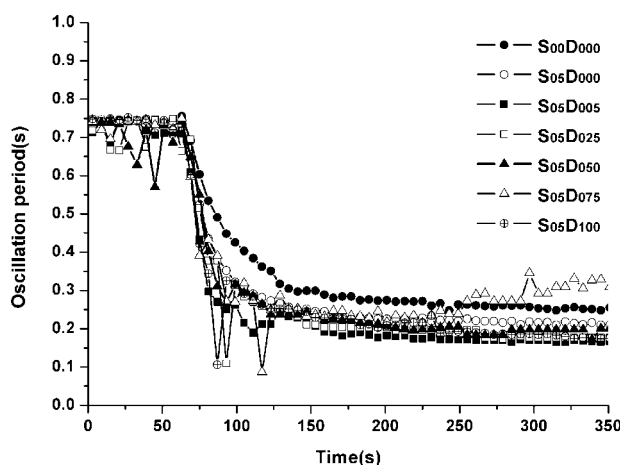


Figure 3 The RPT curves of nanocomposites (0.5 phr nano- SiO_2).

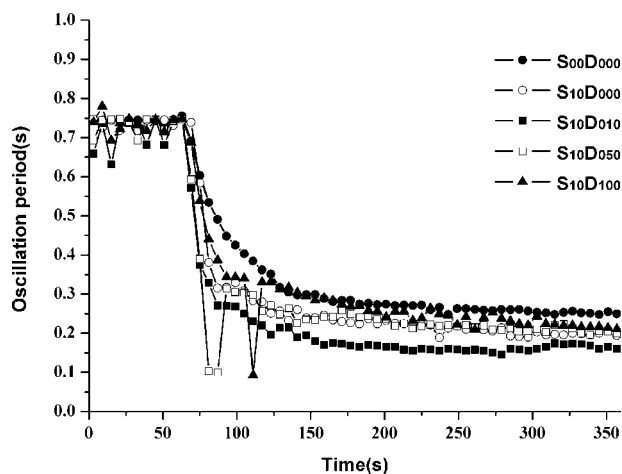


Figure 4 The RPT curves of nanocomposites (1 phr nano- SiO_2).

$S_{05}D_{025}$ was $\sim 340^\circ\text{C}$, and complete degradation temperature was $\sim 507^\circ\text{C}$. It was shown that, addition of dispersant had no influence on the degradation temperature. The initial degradation temperature of $S_{10}D_{100}$ was $\sim 324^\circ\text{C}$, and complete degradation temperature was $\sim 557^\circ\text{C}$. The degradation temperature of $S_{10}D_{100}$ increased about 60°C as compared with the sample $S_{00}D_{000}$. These results showed that the degradation temperature and thermal stability were increased efficiently through adding nano- SiO_2 into TPA/HDDA resin.

Analysis of mechanical properties

According to Cheah et al.,² the tensile strength was increased through adding 20 vol % short-fiber reinforcements. According to Zak et al.,³ the modulus of prototype was increased by adding short glass fiber of 20% volume ratio. However, they used lots of

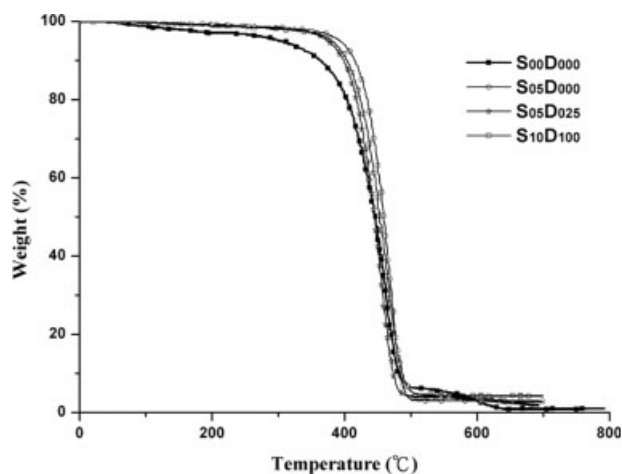


Figure 5 The TGA test results of $S_{00}D_{000}$, $S_{05}D_{000}$, $S_{05}D_{025}$, and $S_{10}D_{100}$.

TABLE II
The Physical Properties of Photopolymer/SiO₂ Nanocomposites

Sample	Tensile strength (kgf/cm ²)	HA (mm)	Volumetric shrinkage (%)
S ₀₀ D ₀₀₀	1.6	48.4	0.02
S ₀₅ D ₀₀₀	2.7	73.3	0.02
S ₀₅ D ₀₀₅	2.9	64.3	0.05
S ₀₅ D ₀₂₅	2.6	70.5	0.06
S ₀₅ D ₀₅₀	2.0	86.7	0.04
S ₀₅ D ₀₇₅	2.7	74.7	0.02
S ₀₅ D ₁₀₀	2.1	81.8	0.02
S ₁₀ D ₀₀₀	2.6	78.1	0.03
S ₁₀ D ₀₁₀	3.2	83.8	0.04
S ₁₀ D ₀₅₀	2.5	73.2	0.04
S ₁₀ D ₁₀₀	1.4	75.9	0.03
S ₁₀ D ₁₅₀	2.3	73.2	0.04
S ₁₀ D ₂₀₀	1.9	79.9	0.07

reinforcements into the photopolymer. We adopted nanocomposites to improve the mechanical properties of photopolymer; the amounts of addition of nanoparticles in our method were only 0.5 and 1 phr.

The results of tensile strength test were listed in Table II, wherein the tensile strength of S₀₀D₀₀₀ was 1.6 kgf/cm². The results showed that addition of nano-SiO₂ can improve the tensile strength. The data of tensile strength were decreased through adding excess dispersant into the mixed resin, such as S₀₅D₀₅₀, S₁₀D₁₀₀, etc. The sample S₁₀D₀₁₀ had the highest tensile strength 3.2 kgf/cm² in this test.

It can be observed from Table II that the hardness of S₀₀D₀₀₀ was HA 48.4 mm. The hardness range between HA 64 and 86 mm showed an increase of about 50% for the samples with additive of nano-SiO₂.

The volumetric shrinkage within TPA/HDDA resin occurs during curing (liquid to solid). The results of volumetric shrinkage were listed in Table II, wherein the volumetric shrinkage of S₀₀D₀₀₀ was

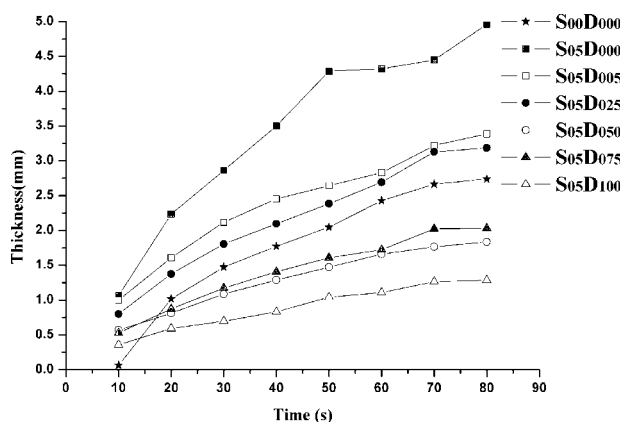


Figure 6 The relationship between curing thickness and exposure time (0.5 phr nano-SiO₂).

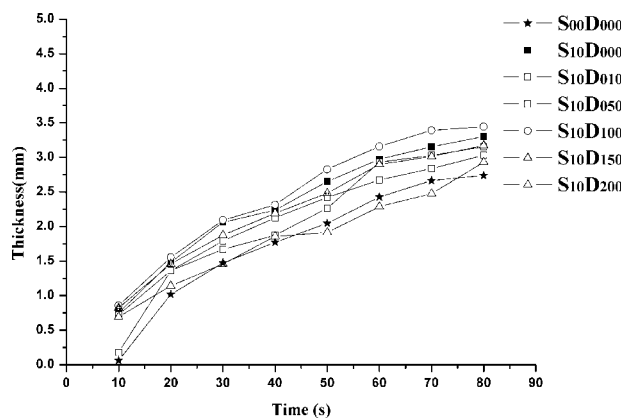


Figure 7 The relationship between curing thickness and exposure time (1 phr nano-SiO₂).

about -0.02%. The difference in volumetric shrinkage between S₀₀D₀₀₀ and other samples were all under 0.05%, therefore the change of volumetric shrinkage was not obvious after adding nano-SiO₂ and dispersant.

Curing thickness and dimensional stability for RP system

According to Benfarhi et al.,⁵ they suggested that the UV-cured resins were synthesized with the additive of clay (3 wt %) to improve the properties. Their UV-cured nanocomposite was used in coating materials. In this article, we applied less amount of nano-SiO₂ (0.5 and 1 phr) into photopolymer. Our major motivation was to improve the physical properties for RP technology applications. Therefore, the curing thickness of manufactured layer and the dimensional shrinkage of prototypes were the concerning properties within RP system.

Figures 6 and 7 depict the relationship between curing thickness and exposure time when the content of nano-SiO₂ is 0.5 and 1 phr. The curing thickness increases with the exposure time, because the crosslinking behavior of photopolymer always proceeds during illumination. The test results show that additive of nano-SiO₂ will increase the curing thickness. As shown in Figure 6, the curing thickness decreases with increasing dispersant concentration when the content of nano-SiO₂ is 0.5 phr. From Figure 7, the variations of curing thickness through

TABLE III
The Dimensional Shrinkage of Photopolymer/SiO₂ Nanocomposites

	Transverse shrinkage (%)	Vertical shrinkage (%)	Thickness shrinkage (%)
S ₀₀ D ₀₀₀	0.60	0.44	0.17
S ₀₅ D ₀₀₀	0.57	1.09	1.06
S ₁₀ D ₀₀₀	0.69	0.72	0.17

adding dispersant in the mixed resin are smaller when the content of nano-SiO₂ is 1 phr. The thicknesses of S₁₀ are more close to S₀₀D₀₀₀'s than S₀₅'s.

From Table III, the dimensional shrinkage of every prototype obtained from various recipes was under 1.09%, namely, the resin was completely cured during processing.

CONCLUSIONS

In this research, the amounts of additives of nanocomposite were much less than those of traditional composite materials. We mixed the nano-SiO₂ 0.5 and 1 phr into the photopolymer to improve the physical properties. The phase separation and the aggregation were reduced with the addition of dispersant in the photopolymer/SiO₂ nanocomposite. For rapid prototyping system, the properties of photopolymer such as curing thickness, tensile strength, hardness, dimensional stability, and volumetric shrinkage were analyzed from experiments. The following was a summary of the findings:

1. If appropriate dispersant is added into TPA/HDDA resin to distribute nanoparticles uniformly, it can efficiently improve phase separation and avoid aggregation phenomenon.
2. RPT test showed that addition of nano-SiO₂ can improve the reaction speed, and lead to a shorter manufacturing time during RP processing. The results of TGA test showed that it was possible to increase the degradation temperature of photopolymer by adding nano-SiO₂ into the composite system.
3. The curing thickness of photopolymer was increased with addition of nano-SiO₂, but it was

decreased by adding dispersant. The tensile strength and hardness can increase by 50% after adding nano-SiO₂ and appropriate dispersant into TPA/HDDA resin. Addition of nano-SiO₂ does not affect the volumetric shrinkage during curing, and the finished prototypes of photopolymer/SiO₂ nanocomposite can have good dimensional stability.

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