Silica Filled Resins for Rapid SLA Tools

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Abstract

A stable silica /SL epoxy resin suspension has been developed at Clemson University. It has been processed to make parts in a commercial StereoLithography Apparatus (SLA). Results of testing show that the composite material has a higher modulus and increased abrasion resistance over the neat epoxy resin. An injection molding die has been made with the reinforced resin in the SLA and tested.

Introduction

StereoLithography (SL) has been used since its introduction in 1988 to build rapid prototypes of solid models out of photo polymers [1]. The solid models were a major development in product design, but not without limitations. Large flat parts would often build with a warp, due to shrinkage of each layer on top of the next. In 1993, 3D Systems released an epoxide based resin, SL-5170, with the intention to reduce curl and shrinkage in parts [2]. SL-5170 was an improvement over previous resins and is widely used in StereoLithography Apparatuses (SLAs) today. However, the mechanical properties of the crosslinked photo resins are different from the thermoplastics that many production parts are made of. Thus, performance tests are difficult to realize with direct rapid prototype (RP) parts.

The need for true prototypes prompted the idea of injecting thermoplastic into dies made in the SLA to produce an RP part made in the production material. In 1996, 3D Systems described the use of SL-5170 (and SL-5180) for building core and cavity inserts for injection molding of a limited quantity of high impact polystyrene parts [3]. Unfortunately, SL-5170 begins to soften at temperatures above 75°C, more than 100 °C below the normal injection temperature of some common thermoplastics, greatly limiting the number of parts (if any) that can be made in an SLA die [3]. However, previous research on particulate filled polymers has established the improvement in the resulting composite properties, including the thermal stability that is important in rapid tooling applications. The objective of this research was to develop a particulate reinforced resin suspension that is suitable for use in an SLA to make core and cavity dies.

Experimental

Materials

Powdered silica was used as a reinforcement in this study. It was added to Ciba Geigy SL-5170 to form a suspension. Viscosity measurements were conducted for the

particulate filled suspension samples at room temperature (73-75°F) using a Contraves Rheomat 15 concentric cylinder viscometer.

Processing

After compounding the suspension, it was introduced into a 3D Systems SLA-250/50 (equipped with a Zephyr recoater). The vat temperature was set to 28°C. Initially, the critical exposure (E_c) and depth of penetration (D_p) were not known for the suspension (the laser scan speed, V_s , was adjusted by varying E_c with D_p held constant in the resin file; V_s is inversely proportional to E_c on the SLA-250/50). Therefore, E_c was set to a high value of 150 mJ/cm^2 in the resin file and a single layer was drawn with success to verify that the resin would cure under laser power.

During subsequent processing trials, two build parameters were of primary concern. First, the scan time per layer, defines the amount of incident energy received by a layer, and is inversely proportional to E_c in the resin file. The second parameter was the time required for an uncured layer to level before being cured by the laser, Z-wait [1]. The first build was conducted using an E_c of 50 mJ/cm^2 and a Z-wait of 25 s. However, it was observed that the 25 s Z-wait did not allow the layers to level. Therefore, the next build was attempted with a longer Z-wait of 60 s, and was successful.

To characterize the composite material thus produced, four ASTM D638 Type I [4] dogbones and six ASTM D695 [5] compression samples were built using the same parameters as the first successful build. A block, 10 mm long, 10 mm wide, and 3 mm thick on a support structure of 0.25 in. was built repeatedly to refine the build parameters. It was observed that a Z-wait of 120 s and an E_c of 20 mJ/cm^2 in the resin file resulted in parts of satisfactory quality. An injection molding die with cavity dimensions specified according to ASTM D638 (Type I) was then processed in the SLA using the reinforced resin suspension with the refined processing parameters.

Characterization

Tensile properties of the particulate composite were investigated using ASTM D638 Type I dogbones. All tests were conducted in an Applied Test Systems (ATS) 900 universal testing machine. Load output was recorded using one channel of a Linseis L6012B 2 channel chart recorder. Three of the samples were tested for strength. The fourth sample was mounted with a Micro-Measurements type EA-50-125AC-350 strain gauge, wired to a Measurements Group P-3500 Strain Indicator. Output from the strain indicator was recorded simultaneously with load from the ATS on the chart recorder.

Injection Molding

Performance of the reinforced material was investigated by testing the ASTM D638 (dogbone) cavity made in the SLA-250/50 in an injection molding machine. An identical cavity was made in the same SLA from neat SL-5170 using standard build

parameters for neat SL-5170 as a control for testing. Both cavities were measured on a CMM coordinate machine (Brown and Sharpe) after postcure.

A standard procedure for finishing and mounting the dogbone die had been established with previous dies made in neat SL-5170. Approximately 20 mils of material was removed from the back of the SLA die for fitting into a Master Unit Die (MUD) frame using a belt sander. This proved ineffective for the reinforced resin die because of the high abrasion resistance. Consequently, a milling machine was used.

Injection molding was done in an Arburg 221-55-250 Allrounder 28 ton injection molding machine. Both dies were mounted in the Master Unit Die frame on the ejector side of the clamp. Because the "core" side of the dogbone was flat, a MUD insert made of tool steel was used. Six ejector pins were used in each die, two of which were fitted with thermocouples wired to a Linseis L6012B 2 channel chart recorder. Both MUD frames were cooled with city water (25°C). Manual cycle was used because flash caused parts for both dies to hang on an ejector pin during ejection. Cooling time was set at 30 seconds; actual cycle time was approximately 45 seconds which varied slightly because parts were removed by hand from the sticking ejector pin. General purpose polystyrene (GPPS) was injected at a temperature of 220°C and an injection pressure of 8000 psi.

Results and Discussion

Suspension Viscosity

Adding a solid reinforcement raises the viscosity of a liquid resin. Therefore, viscosity tests were first conducted to obtain an understanding of the flow characteristics of the suspension. *Figure 1* displays the viscosity of the suspension as a function of shear rate. The viscosity does not change significantly within the shear rate range of 2.5 s^{-1} to 25 s^{-1}. At a nominal shear rate of 15 s^{-1}, the viscosity of the suspension is 1500 cP. This

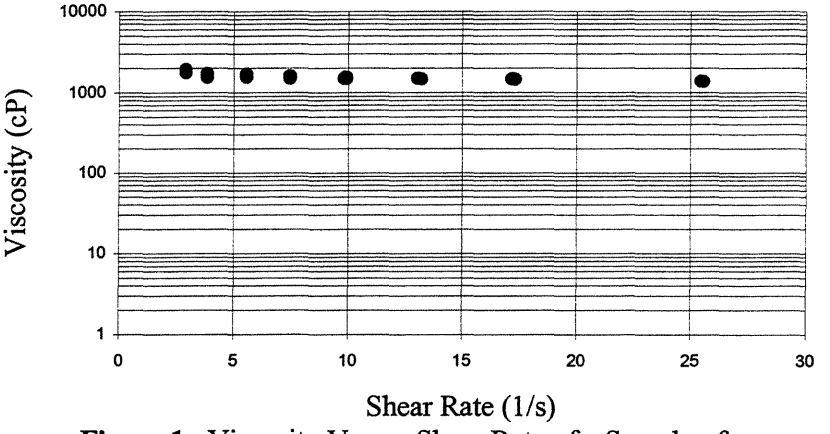

Figure 1. Viscosity Versus Shear Rate of a Sample of Reinforced Resin Suspension from the SLA-250/50 Vat.

value is about five-fold higher than that of 235 cP for the pure resin [6] and justifies the

longer Z-wait needed for the particulate suspension as compared with that for the pure resin.

Several equations have been proposed in the literature to predict the viscosity of suspensions [7]. *Figure 2* displays the predictions for the viscosity ratio (η/η_o) as a function of the weight fraction of the particulates using the Einstein, Mooney, and

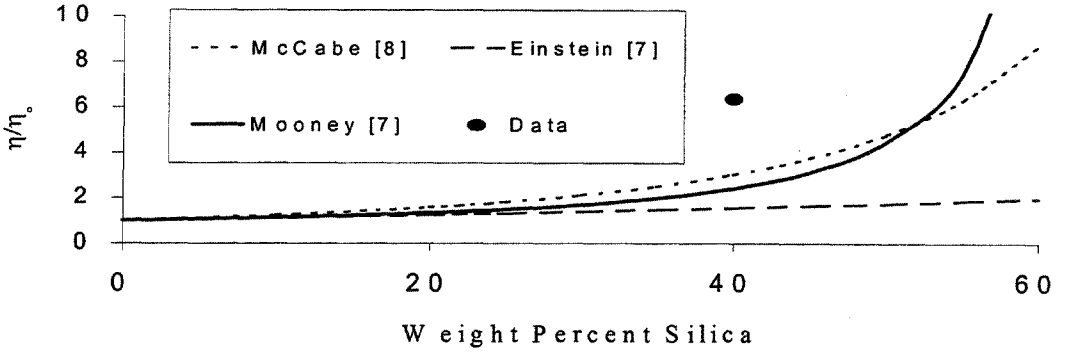

Figure 2. Comparison Between Empirical Equations for Estimating Viscosity of the Suspension and Experimental Data

McCabe [8] equations. The actual viscosity of the suspension is approximately twice that of the highest prediction. The most probable reason for the discrepancy is the agglomeration of the particles. It is known that agglomeration can lead to a viscosity ratio increase (at a fixed weight percent of particulates) of as large as 8 [7].

Stability of Suspension

Viscosity for samples from the SLA vat are shown over a 21 day period in *Figure 3.* Although the viscosity in the vat decreased slightly during the period, the actual change was less than 15% of the original value. A possible reason for the change in viscosity is the settling of particles during storage, a phenomenon that needs further investigation. However, the degree of settling was within useful limits.

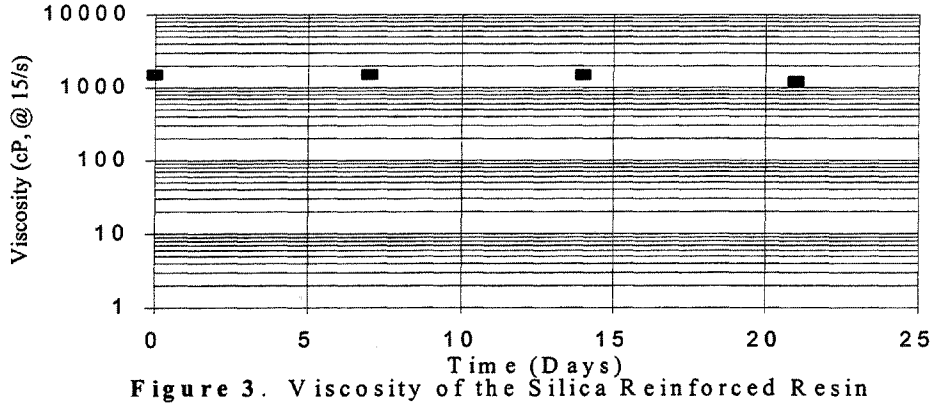

Figure 3. Viscosity of the Silica Reinforced Resin Over a 21 Day Period.

Processing in the SLA

Parts built with a Z-wait of 60 s in the reinforced resin exhibited a convex surface in the XY plane. This effect was a result of the laser scan commencing before the liquid resin had leveled off after recoating. As illustrated in *Figure 4*, a Z-Wait of 120 s eliminated the convex surface. However, because the convex layers of the part cured together properly even with a Z-Wait of 60 s, it is believed that the scan speed of the laser can be increased when building parts with a Z-Wait of 120 s due to the fact that there is less resin per layer to be cured.

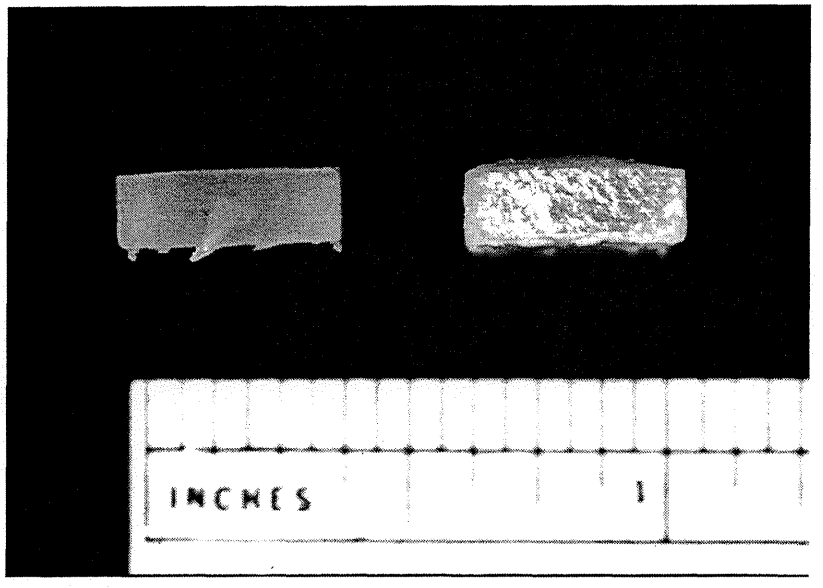

Figure 4. Sectional views of reinforced resin samples made at two different Z-waits – left: 120 s, and right: 60 s.

Dimensional Accuracy

Scattering of the laser beam by the reinforcement phase occurs because the refractive index of the silica is not identical to that of the resin [9]. This phenomenon is clearly seen with the naked eye during part building and was cause for some concern. If the beam scatters, a wider path is expected to be exposed to UV in the line drawn on the resin surface. The wider path drawn in the resin may affect part accuracy in the X and Y directions. The issue has not been fully investigated, but data for measurements on the cavity of the ASTM D638 Dogbone die are presented in *Table I.* Errors between the ASTM D638 CAD file specification and the actual SLA part were no larger for the reinforced resin than for the neat resin.

Table I. Dimensions of ASTM D638 Die Cavity

Dimension	Specification (in.)	Neat SL-5170 (in.)	Filled SL-5170 (in.)
Gauge Width 1	0.500	0.507	0.496
Gauge Width 2	0.500	0.507	0.496
Gauge Width 3	0.500	0.507	0.496

Injection Molding

The ASTM D638 Type I cavity die processed in the SLA using the reinforced resin was compared to an identical cavity die processed in the SLA using neat SL-5170. This test was performed to ensure that the composite material could, in fact, be used for rapid tools. Both the composite tool and the neat tool made 100 parts with no significant damage to the tool. The composite tool lost two small chips, one during ejection of part numbered 42 and the second during ejection of part numbered 49. The neat tool lost one chip during the ejection of part numbered 30. The temperature of both dies rose to 37°C after 10 molding cycles and remained steady thereafter.

The quality of parts leaving the mold did not appear to change (with the exception of the chips) during the test for both tools. *Figure 5* displays both the composite and the neat tools after testing along with parts numbered 12 and 100 from both tools. The parts injected in the composite tool appear opaque from the rough surface of the particulate reinforced resin.

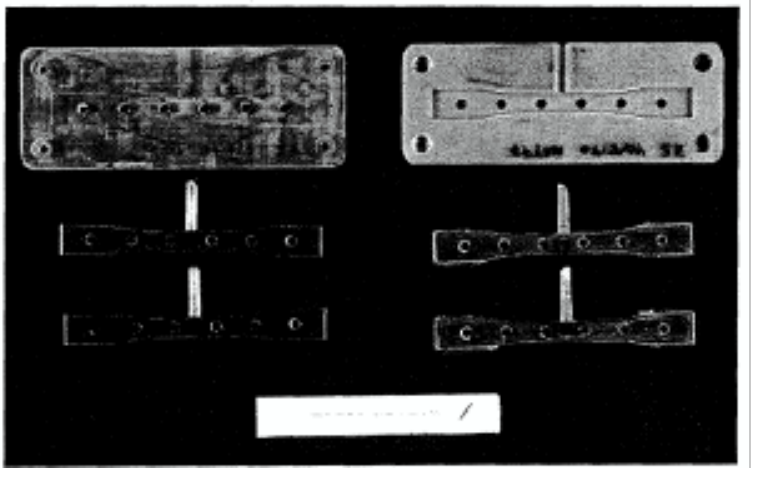

Figure 5. The neat SL-5170 ASTM D638 Die with 2 parts (left) and the reinforced SL-5170 Die with 2 parts (right).

Composite Material Characterization

The tensile strength of a particulate reinforced resin, σ, is expected to be less than the equivalent unreinforced resin tensile strength, σ_o, according to the equation

$$\sigma = \sigma_o(1 - (\frac{\phi_p}{\phi_m})^{\frac{2}{3}})$$

where ϕ_p is the volume fraction of the reinforcement and ϕ_m is the maximum packing content which can be assumed 0.6 for random loose packed spheres [10]. ϕ_p is 0.22 for 40 weight percent silica in SL-5170. According to the equation, it is expected that SL-5170 would lose 51% of its original strength after adding reinforcement. However, strength data, presented in *Table II*, indicated that the composite has a tensile strength of 48 MPa, a loss of only 20% as compared to that of neat SL-5170 [6]. A possible reason for the higher strength (than what is predicted) is the shape of the particles. Deviation from spherical shape toward an elongated shape will result in higher strength values.

Tensile modulus is expected to increase with the addition of particulate reinforcement. Quantitative estimates can be made using mechanical property data for the reinforcement phase and the resin phase (*Table III*). The estimated tensile modulus according to SMC, a program developed at the University of Delaware, is 4400 MPa compared to an experimental value of 2300 MPa for neat SL-5170 [6]. Experimental data indicated a tensile modulus of 4300 MPa for the reinforced photo polymer. It is expected that the more than 80% increase in the modulus (with the addition of particulates) will increase the creep resistance of the composite and will lead to an increase of the heat deflection temperature of the composite over that of the pure resin. These properties will be investigated in future work.

Table II. Properties of Composite

Property	Predicted	Experimental
Density (g/cm^3)	1.55	N/A
Tensile Modulus (GPa)	4.4	4.3
Tensile Strength (MPa)	30	48
Coefficient of Thermal Expansion (ppm/K)	55	N/A

Table III. Physical Properties of Silica and Ciba Geigy SL-5170

Property	Silica	Ciba Geigy SL-5170
Density	2.65 [11]	1.14 (uncured) 1.215 (cured) [6]
Refractive Index	1.55 [11]	1.49 (uncured) 1.53 (cured) [6]
Tensile Modulus (GPa)	73 [12]	2.3 [6]
Tensile Strength (MPa)	3400 [12]	60 [6]
Thermal Conductivity (W/m-K)	1 [12]	0.2002 [6]
Coefficient of Thermal Expansion (ppm/K)	5 [12]	90 [6]

Conclusions

The following conclusions are drawn from this study:

1. A silica/ epoxy suspension was used to make parts in a commercial StereoLithography Apparatus (SLA).
2. The composite material has an 80% higher modulus and increased abrasion resistance as compared to the base resin, and yet it retains about 80% of the strength of the base resin.

Acknowledgements

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