

Binder Development for Indirect SLS of Non Metallics

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Abstract:

In this work, a binder system for non metallics such as graphite has been developed and tested. A graphite-phenolic mixture was used for making bipolar plates using SLS. Phenolic resin melts (~90°C) instead of cross-linking (~165°C) in the SLS machine. During post processing in a furnace, the SLS parts slumped due to remelting of phenolic resin with no other binder present to hold the powder together. To prevent this slumping and to increase the green strength of the SLS parts, a new binder system was developed with Nylon/11 added. Nylon/11 has a melting point of ~185°C and is able to hold the SLS part together until the phenolic can cross link, preventing slumping. Single layer scan experiments with different compositions and SLS parameters were run to identify optimum composition and SLS parameters. Three point bend specimens were prepared with 70 wt. % Graphite-25 wt. % Phenolic- 5 wt. % Nylon/11 and 70 wt. % Graphite-20 wt. % Phenolic- 10 wt. % Nylon/11, tested and compared to graphite-phenolic parts. No significant increase in green strength was attained with Nylon/11 addition.

1. Introduction:

In indirect selective laser sintering (SLS) high melting temperature materials like metals and ceramics are coated or mixed with polymers and are then processed in the SLS machine. Under the laser power, these polymers melt and bind the inorganic materials together. Successful use of metals and ceramics in SLS process depends on successful development of binders.

Commercially, there are few material systems such as Laserform™ A6 steels available which are tool steels coated with unspecified binders [1]. These binders serve as sacrificial binders in that they are useful only in the initial stages: processing in the SLS machine and to the start of furnace sintering. Once sintering starts, the component/part gets strength from sintering and these binders are eliminated by high temperature burnout. There are some applications wherein sintering is difficult as in the case of graphite/SiC and a binder that can give strength during all the stages of processing either by remaining as itself or by transforming to some other state is needed. One such application is the fabrication of graphite bipolar plates or current collectors in fuel cells.

Research has been done on development of binders for graphite bipolar plates [2] and SiC composites and wafer carrier plates [3, 4]. Chen [2] used Phenolic resin as a binder. The Phenolic resin was pre-mixed with a hardener/ catalyst and was purchased from Georgia Pacific. Novalac was the resin and had HMTA or hexamine was the catalyst. The green strength of the Graphite-Phenolic parts was not good. The green strength values were not reported. After infiltrating with some resin such as epoxy after furnace curing, the parts gained strength. Bhandari [3] tried to improve the green strength of SiC parts by adding Nylon and Wax in addition to Phenolic resin. Trials/experiments were done outside the

SLS machine by mixing powders, making three point bend specimens and heating them in a furnace at $\sim 140^{\circ}\text{C}$. Green strength in the range of ~ 7 - 19 MPa was achieved. It is difficult to get such a long exposure to temperature in a SLS machine. A value of 2 MPa will ensure that the parts have adequate strength to be handled.

Another motivation in identifying a suitable binder composition is that Phenolic melts ($\sim 90^{\circ}\text{C}$) before it can cross link ($\sim 165^{\circ}\text{C}$) as seen in the DSC plot below [2].

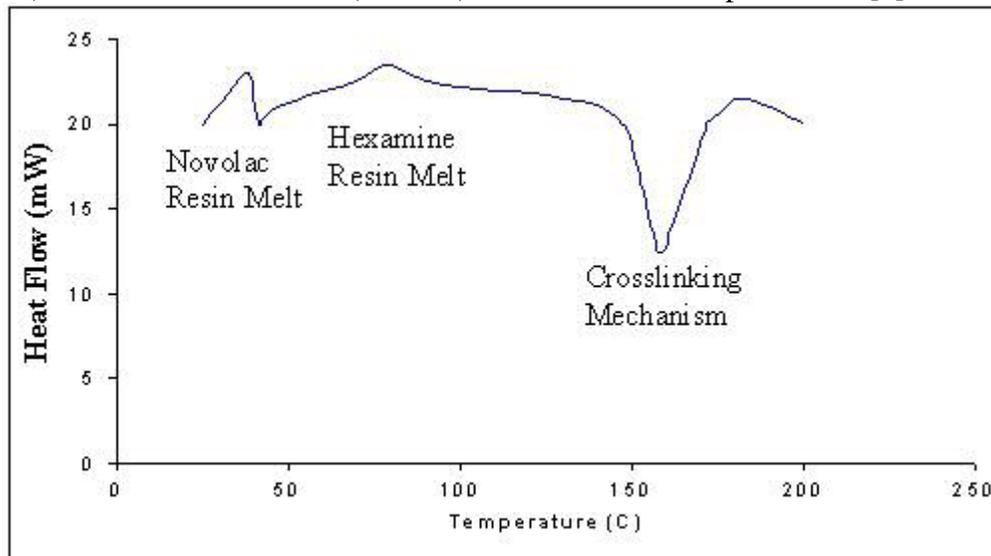


Figure 1: DSC plot of Phenolic resin [2] shows the resin melts much (50 - 90°C) before cross linking occurs (~ 150 - 160°C)

During post processing in the furnace, the SLS parts slump due to remelting of the phenolic resin with no other binder to hold the powder together. To prevent this slumping and improve the green strength, its necessary to identify some binder composition that can hold the powder together in the range of 90 - 165°C . Nylon 11 has a melting point of $\sim 185^{\circ}\text{C}$, so it can be used to retain the shape in that temperature range.

2. Experimental:

The graphite-Phenolic resin- Nylon/11 were mixed with different composition and heated in a oven to $\sim 200^{\circ}\text{C}$. Based on the nature of the mix (how hard or soft they were), specific compositions were identified to be suitable for further processing. These compositions were then used in single layer scan experiments in the SLS machine DTM sinterstation 2000 to identify optimum process parameters. Based on these results, 3 point bend specimens were prepared.

2.1 Materials:

Graphite (GS 150 E) was purchased from Graftech International. Phenolic resin (Durite AD 332 A) was purchased from Hexion in a premixed condition. Nylon/11 was purchased from Rilsan Fine Powders.

Graphite- Phenolic-Nylon were mixed in the following ratio, placed in a oven and heated to ~200°C to observe the nature of the mix:

Graphite (wt%)	Phenolic (wt%)	Nylon11 (wt%)	Remarks
70	30	0	Base composition
70	25	5	
70	20	10	
70	15	15	

Table 1: Initial compositions used in oven test

Of these, 5 & 10% Nylon addition made the mass harder than the base composition and 15% Nylon addition made the mass softer than the base composition. Based on these experiments, we identified that 5% & 10% Nylon 11 addition as two potential compositions.

2.2 Single layer scan experiments:

To confirm the behavior of these mixes in the SLS machine under laser power and to minimize the use of powder, single layer scan experiments were performed with different laser power to identify optimum laser parameters. Single layer scan experiments were done in a DTM Sinterstation 2000. The build height was kept at 0.003 inches and the powder layer thickness was kept at 0.004 inches to prevent the rollers from moving. Graphite powder was mixed with different binder composition and laid on a graphite plate on the partbed. In all the experiments, the weight ratio of Graphite to binder was kept at 70:30. This composition was identified by Chen [2]. The compositions used for single scan experiments were same as shown in table 1.

SLS parameters used:

For Single layer scan experiments, the partbed temperature was kept at 80°C and the feed bin temperature was kept at 45°C. Fill Laser powers used were 7, 12, 17 W (12 W was identified to be optimum by Kaushik [5]) and an outline laser power of 4 W was used.



Part bed for single layer scan expt



A single layer scan in progress

Figure 2: Single layer scan experiment in DTM sinterstation 2000.

Different shapes were created using different laser power. Ability to produce sharp features, relative green strength to handle the single layer scan parts and absence of curling or delamination were the metric used to identify the suitability of a particular binder composition.

2.3 Three point bend specimens by SLS process:

2.3.1 5 wt. % Nylon:

2.3.1.1 Powder preparation:

Based on the results from single scan experiments, the 5% Nylon (Graphite: 70 wt% - Phenolic: 25 wt% - Nylon: 5%) mix was processed on a scale enough for a build in the SLS machine. The powders were mixed in the above proportion in a ball mill with alumina media for 24h. The powders were sifted to remove coarse particles and were filled in the SLS machine.

2.3.1.2 SLS Build:

Three point bend specimens (5 in X 0.5 in X 0.125 in) were prepared using 12 and 14 watts laser power (identified by single scan experiments). Samples did not have acceptable strength and broke during removal from the partbed. A new build was made using the following laser powers: 18 W, 22 W, and 26 W. Four or five specimens were made with each laser power. Two builds were made to assess the repeatability.

2.3.2 10 wt. % Nylon:

2.3.2.1 Powder preparation:

The 5% mix prepared for previous builds was modified to 10% Nylon composition by adding extra Nylon/11 & graphite. The 5% mix was sifted, new additions (extra graphite and Nylon/11) were made and the mix was ball milled for 24 h. The mix was again sifted to remove any large lumps of powder.

2.3.2.2 SLS build:

Three point bend specimens (5 in X 0.5 in X 0.125 in) were prepared using 22, 26, 28 and 30 watts laser power. 22 & 26 W were used in the 5 wt. % Nylon experiments. 28 & 30 W were used to see if increasing the laser power had an effect on the strength. The partbed temperature was kept at 80°C and the feed bin temperature was kept at 45°C. The outline laser power was 4 watts.

Four or five specimens were made for each laser power in each build. Three builds were made in all to assess the repeatability.

2.4 Mechanical characterization:

The specimens were tested in a 5 kN Instron machine (Model 3345) with three point bend setup as shown in Figure 3.

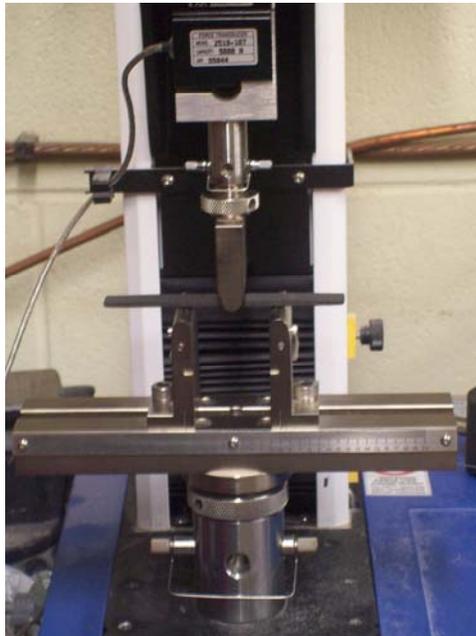


Figure 3: A three point bend test setup.

The span length was set at 50 mm and a displacement rate of 0.1 mm/min used. A Flexure stress versus flexure strain plot was obtained in all the tests and the maximum flexure stress was reported as the flexure strength.

3. Results:

3.1 Single layer scan experiments:

Figure 4 below shows the single scan layers (the numbers in the figures denote the wt. % of Graphite, Phenolic, nylon/11 respectively).



Figure 4: Single layer scan parts with different binder composition

All the binder compositions were able to produce the features and none had any curling or delamination. The dimension of the parts were measured and compared to the dimensions of the input drawing. 15% Nylon showed more shrinkage than the rest. The strength of nylon- added parts was relatively better than graphite-phenolic parts. Some graphite-phenolic parts broke while trying to remove them from the partbed, while the nylon- added parts did not break. This showed that there was some relative improvement due to Nylon addition.

Based on these results, 3 point bend specimens were built with 5 wt. % Nylon and 10 wt. % Nylon additions.

3.2 Three point bend test results:

3.2.1 5 wt. % Nylon mix:

Stress - strain plots of 5% Nylon mix with different laser power are shown in the Figures 5 and 6 below:

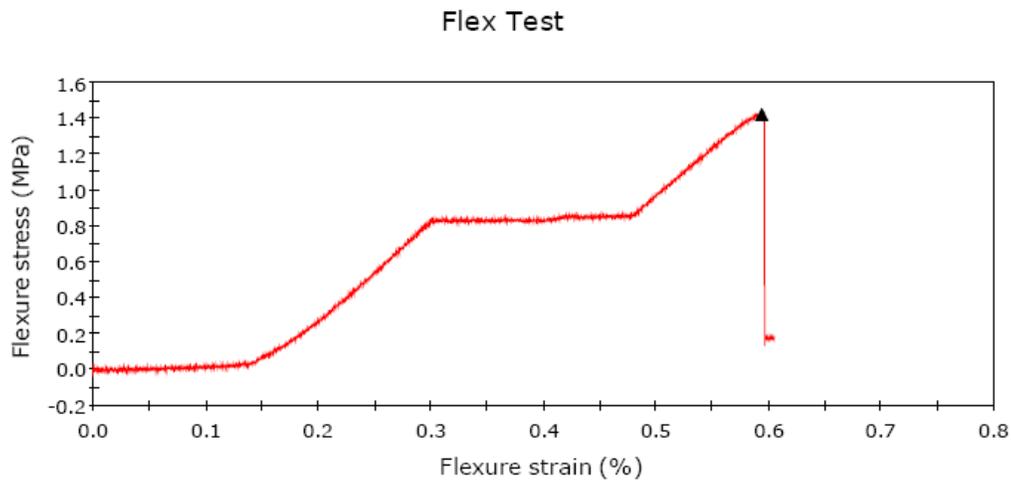


Figure 5: A typical 5% Nylon mix with 22 W fill laser power. The flexure strength of this specimen is 1.42 MPa.

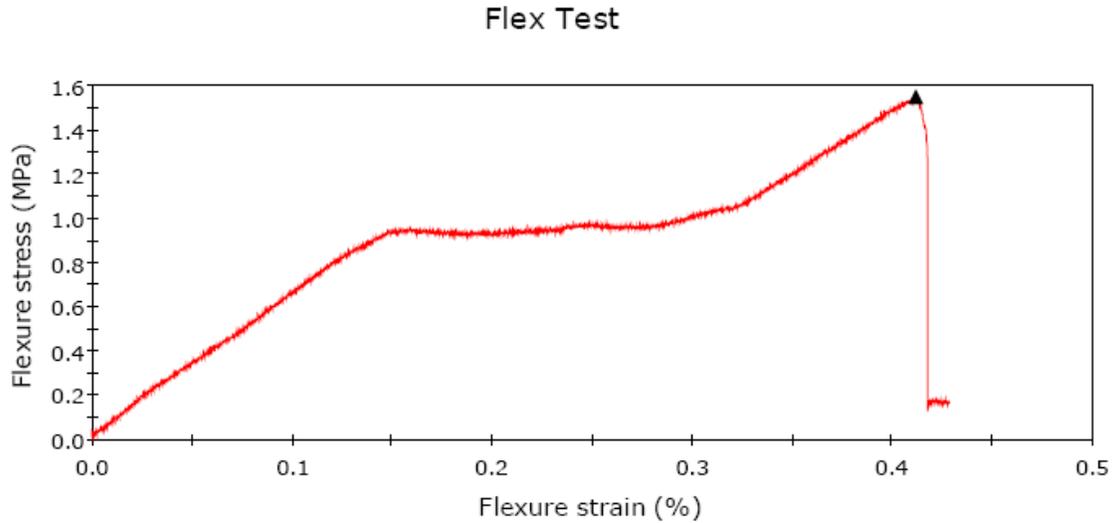


Figure 6: A typical 5% Nylon mix with 26 W fill laser power. The flexure strength of this specimen is 1.54 MPa.

It was found that 5% Nylon addition did not improve the green strength dramatically. The green strength of compacts used in power metallurgy is around 7 MPa [6]. This 7 MPa green strength enables the compact to be handled. A realistic target of 4-5 MPa was set which should be sufficient enough to excavate the parts from the partbed and transfer them to the furnace.

3.2.2 10 wt. % Nylon addition

The flexural stress-flexural strain plots for different laser powers are shown in Figure 7 (22 watts), Figure 8 (26 watts), Figure 9 (28 watts) and Figure 10 (30 watts). The associated tables list point values. (Note: the difference in the shape of the curve was due to the different pre-loading used before the start of the test).

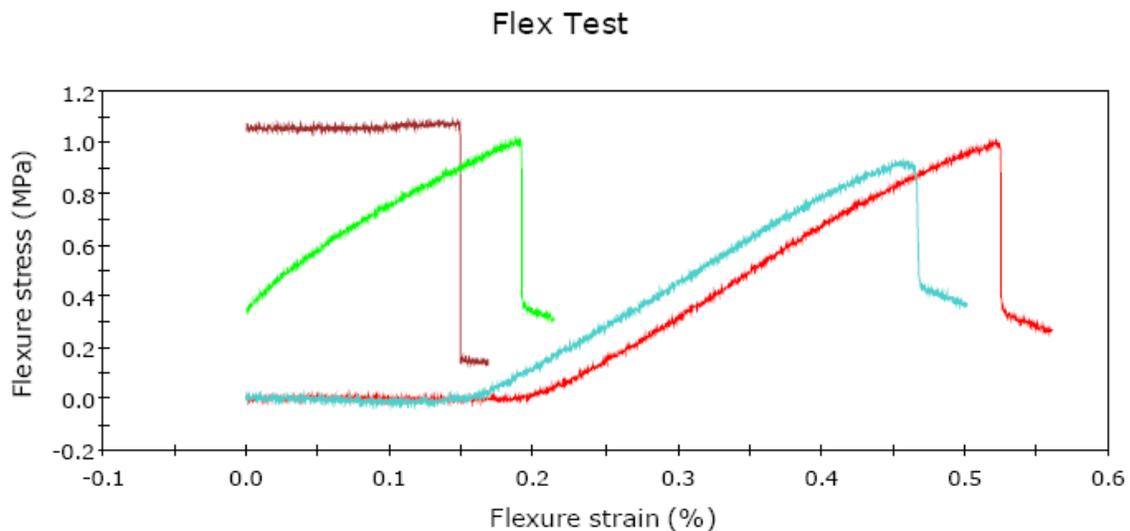


Figure 7: Flexural stress-strain plots of 3 point bend specimens made with 22 watts laser power.

	Maximum Load (N)	Maximum Stress (MPa)
1	2.65	1.00
2	3.00	1.09
3	2.31	1.01
4	2.14	0.93
Mean	2.53	1.01
Standard Deviation	0.37841	0.06474
Minimum	2.14	0.93
Maximum	3.00	1.09

Table 2: Flexural load and stress values of 3 point bend specimens made using 22 Watts laser power & 10 wt. % Nylon

Flex Test

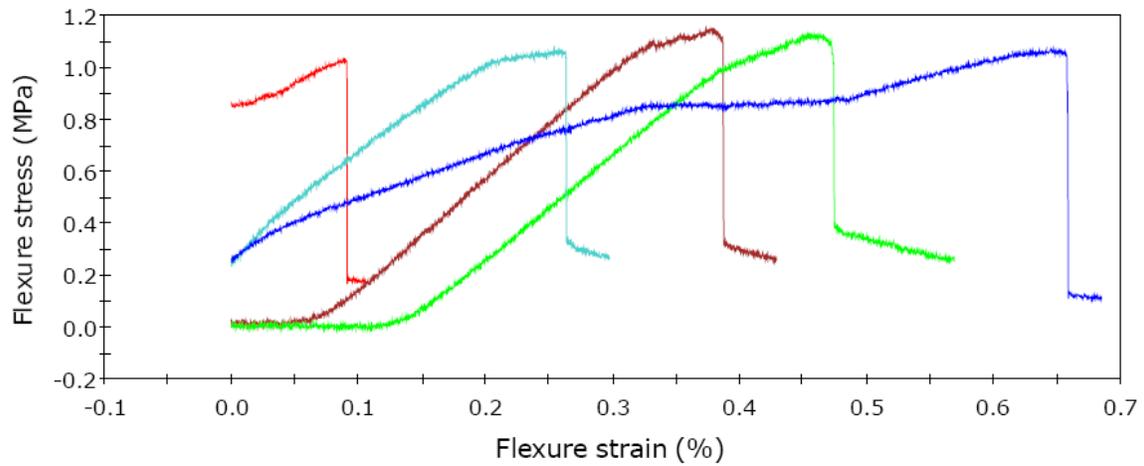


Figure 8: Flexural stress-strain plots of 3 point bend specimens made with 26watts laser power.

	Maximum Load (N)	Maximum Stress (MPa)
1	3.63	1.03
2	2.86	1.15
3	2.95	1.13
4	2.93	1.07
5	3.75	1.07
Mean	3.23	1.09
Standard Deviation	0.43000	0.04829
Minimum	2.86	1.03
Maximum	3.75	1.15

Table 3: Flexural load and stress values of 3 point bend specimens made using 26 Watts laser power & 10 wt. % Nylon

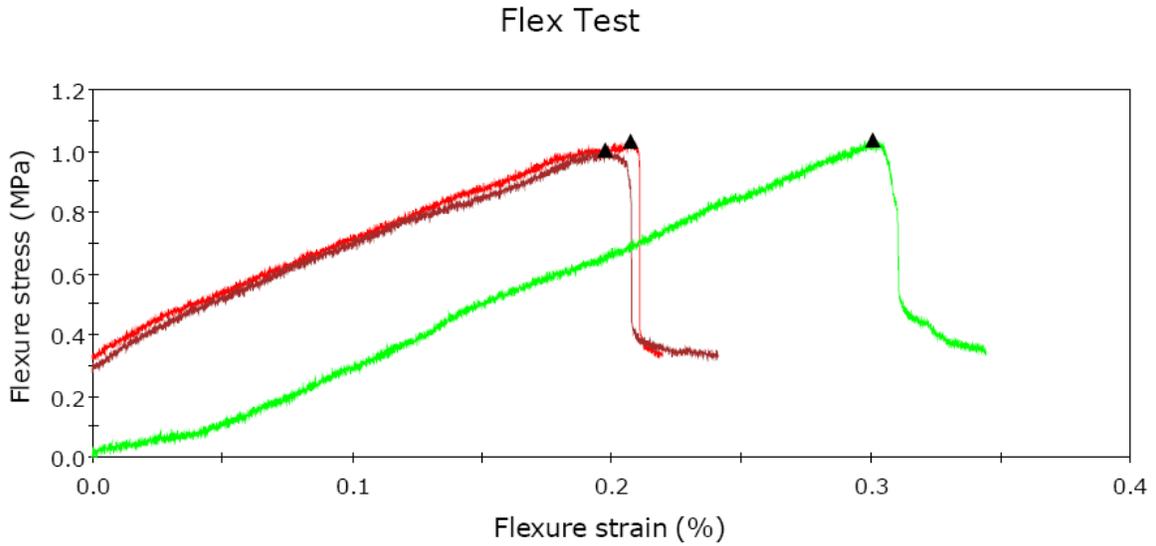


Figure 9: Flexural stress-strain plots of 3 point bend specimens made with 28watts laser power.

	Maximum Load (N)	Maximum Flexure stress (MPa)
1	2.30	1.03156
2	2.15	1.00472
3	2.00	1.03642
Mean	2.15	1.02423
Standard Deviation	0.14564	0.01707
Minimum	2.00	1.00472
Maximum	2.30	1.03642

Table 4: Flexural load and stress values of 3 point bend specimens made using 22 Watts laser power & 10 wt. % Nylon

Flex Test

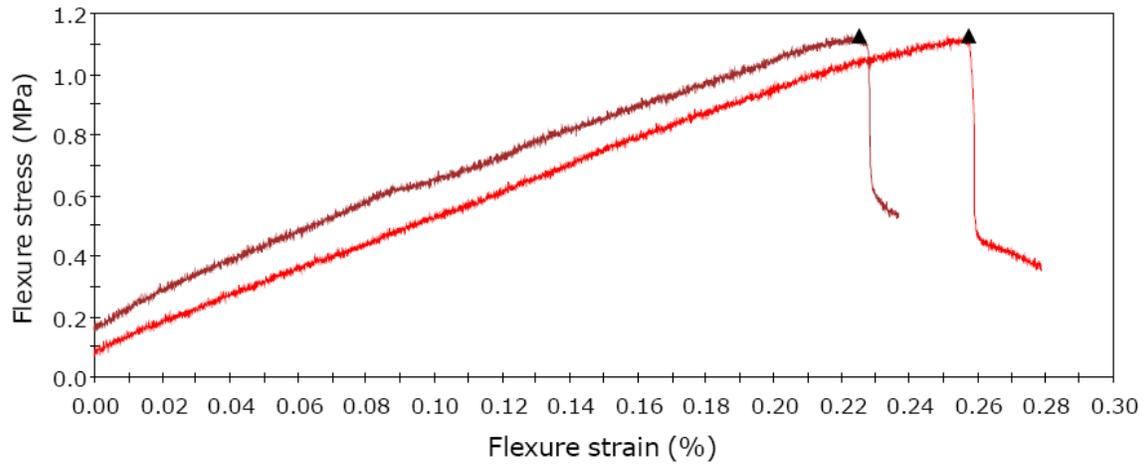


Figure 10: Flexural stress-strain plots of 3 point bend specimens made with 30 watts laser power.

	Maximum Load (N)	Maximum Flexure stress (MPa)
1	2.55	1.12694
2	2.45	1.12625
Mean	2.50	1.12659
Standard Deviation	0.07636	0.00049
Minimum	2.45	1.12625
Maximum	2.55	1.12694

Table 5: Flexural load and stress values of 3 point bend specimens made using 30 Watts laser power & 10 wt. % Nylon

The flexural strength of 10 wt. % Nylon specimens was ~1 MPa. Increasing the Nylon/11 content degrades the strength values.

3.3 Carbonization experiments

To observe the slumping behavior of the green parts, four nylon added specimen were put in a high temperature vacuum furnace along with two graphite-phenolic parts. They were heated to 1200°C. All the parts slumped as shown in figure 11. Nylon/11 additions didn't help in preventing the slumping.



Figure 11: 3 point bend specimens in the furnace before and after vacuum furnace processing. All the parts were slumped after carbonization at 1200°C.

Some carbonized samples were tested for the brown flexural strength. All the brown (carbonized) parts showed an increase in flexural strength (~2.5-2.75 MPa). A typical flexure stress- flexure strain plot of the brown parts is given below:

Flex Test

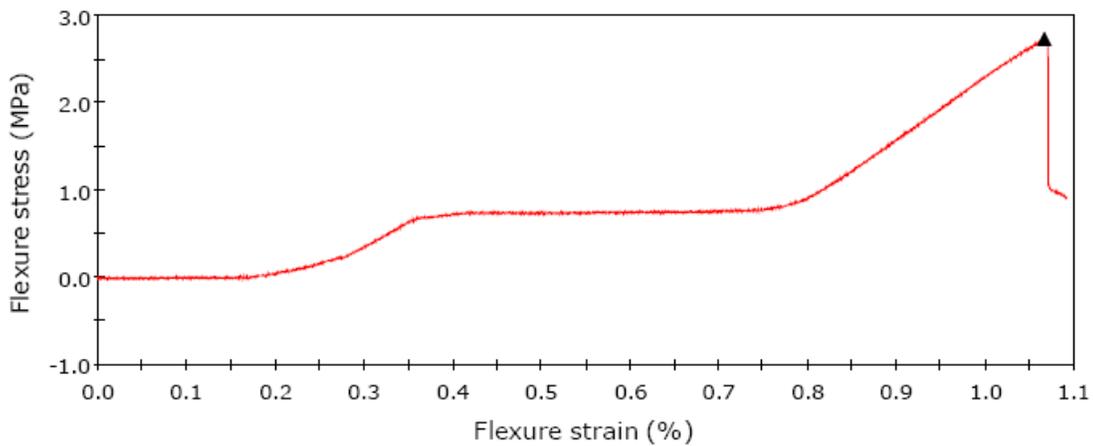


Figure 12: A typical flexure stress- flexure strain curve for a brown (Carbonized) part. The flexural strength of the brown parts was in the range of ~2.5-2.75 MPa.

4. Discussion:

Both the 5 wt. % and 10 wt. % Nylon specimens had a flexural strength of ~ 1-2 MPa. Higher addition of Nylon/11 apparently degrades the strength. This value is comparable to the green strength value of LaserForm™ Tool steel of 3D systems. LaserForm™ has Phenolic, Nylon and wax in its binder composition and has a green strength of 1-2.1 MPa. This could be the maximum possible strength value with this composition. Higher strength could possibly be achieved only by a significant change/ new additions to the binder composition.

Also, the particle size of the Phenolic resin could be another factor that influenced the green strength adversely. The earlier experiments [2, 5] used cryomilled phenolic resin, which had particle sizes in the range of ~10-15 microns. The phenolic resin used in this experiment was unmilled with particle size in the range of ~31 microns. So, the phenolic particle size would have nullified the nylon effect. Scanning electron microscope images of some of these specimens were obtained to see if there was any difference between the milled and un- milled resins' binding behavior.

The SEM images of a specimen prepared using milled phenolic powder are shown in the Figure 13 below:

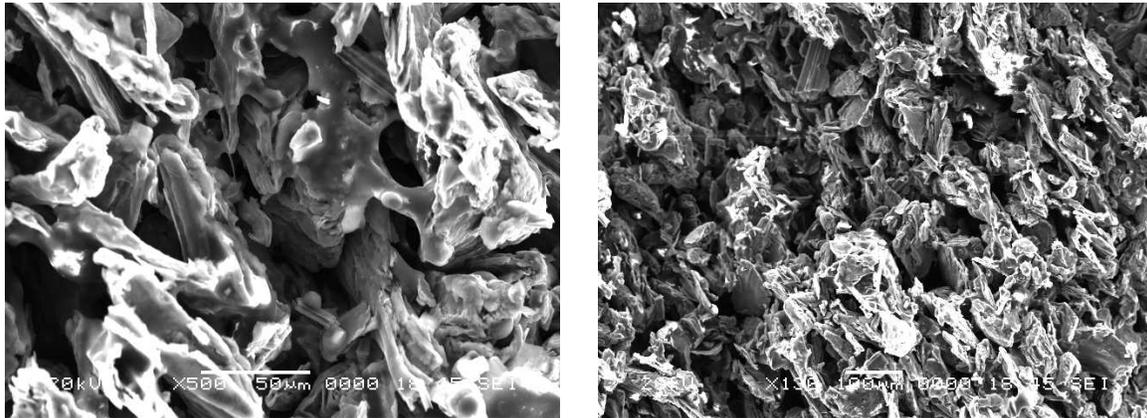


Figure 13: SEM images of a specimen prepared using milled phenolic resin. Note the dispersion of the resin is uniform and no big globs of molten resin seen.

The SEM images of a specimen prepared using un-milled phenolic powder are shown in the Figure 14 below:

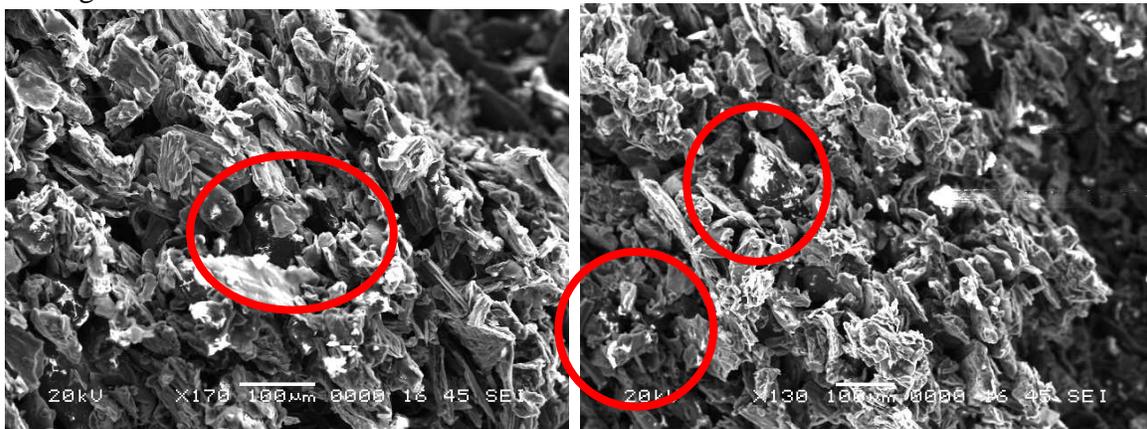


Figure 14: SEM images of a specimen prepared using un-milled phenolic powder. Note the large globules of molten resin seen, marked by red circles.

The milled resin sample did not have any large molten globules. But the un-milled resin sample had large molten globules indicating that the dispersion behavior was different.

5. Conclusion:

It appears that Nylon addition up to 10% does not provide improvement in the green strength of the SLS graphite parts. Nylon/11 addition also does not prevent slumping. One possible reason for this behavior (effect on strength) could be due to the initial particle size of the powder. Phenolic resin used by Chen [2] & Kaushik [5] was cryogenically milled to 10-15 micron size whereas the resin used in this work is unmilled and was around 31 microns. Particle size has an effect on the sintering behavior and so on the green strength. Reducing the phenolic resin particle size, addition of acrawax resin to the composition and efforts to induce cross-linking inside the SLS machine are future plans to improve the green strength.

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