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Polymer Composites Reinforced by Carbon-Allotrope Fillers for Selective Laser Sintering (SLS) – A Review

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ABSTRACT: The limited commercial availability of applicable polymer powders has hindered the widespread implementation of SLS as a legitimate manufacturing method.[1] This is partly due to the mechanism of SLS, which requires powders to meet rigid specifications if processing is to be successful. Furthermore, powders that do meet requirements are often incapable of producing quality, high-performance parts. Academic and industrial research has focused on composite development to overcome this problem.[2] The incorporation of fillers including calcium carbonate, molybdenum disulfide, and aluminum have all been found to influence the processing behavior of PA12 powder and ultimately, the properties of the final part.[3-5] Here, the thermal and mechanical properties of sintered composite parts produced using polymer powders reinforced by various carbon-based fillers is discussed.

INTRODUCTION

Selective Laser Sintering (SLS) is a production technique that uses a "layer-by-layer" mechanism to construct complex geometric parts. SLS is classified as a Powder Bed Fusion (PBF) process, one of roughly a dozen distinct layering technologies known collectively as "3D-Printing" and allocated to the field of Additive Manufacturing (AM).[6] In direct contrast to conventional "reductive" manufacturing, which typically involves hand-tooling to remove excess material, the required manpower and waste generated via AM is minimal. Thus, AM is becoming increasingly popular as a simplified and efficient approach to industrial production.

SLS Mechanism

As part of the PBF family, the basic mechanism behind SLS is literally implied; a bed of powdered material is fused together to form the final part or "build." The SLS machine comprises a build platform, powder bed, laser source, laser optics, feed cartridges, and a blade or roller for powder leveling (Figure 1).[7]

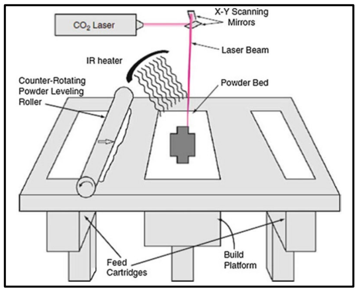


Figure 1. Schematic of the selective laser sintering machine.[7]

The SLS process consists of three fundamental steps that are repeated until the final layer of the part has been sintered.[7]

(1) **Powder Deposition**: Feed cartridges affixed to the build platform deposit the selected material onto the powder bed. The bed is preheated to a temperature just below the melting point of the powder, referred to as the "build temperature' and denoted T_B. The bed is held at T_B throughout the subsequent steps until the part is complete.[8,9] Both initially and between each consecutive sintering layer, a blade or roller disseminates the powder evenly across the bed to ensure proper surface leveling and preserve the integrity of the final part.[7]

(2) **Powder Solidification**: The laser optics scans and predicts the processing area in accordance with dimensions defined by a computer-aided design (CAD) model. The appropriate superficial region is then exposed to the laser source; for industrial SLS systems, this is conventionally a 10.6 µm carbon dioxide beam, but for benchtop machines, a diode or fiber laser is employed. The targeted particles respond by softening, melting, and solidifiying.[7]

(3) **Platform-Lowering**: The build platform lowers by one layer thickness and the procedure is repeated. Once the final layer has been sintered, the chamber is slowly cooled to the build extraction temperature, T_E.[7]

Applicable Materials

The scope of materials applicable to SLS can be divvied into three groups based on chemical nature: plastics (polymer-based powders), metallics (metal powders), and ceramics (ceramic powders). Though they are molecularly very different, significant overlap exists in the industrial end-use applications between the groups. All three are used in the aerospace, automotive, dental, jewelry, oil and gas, and tooling industries, among others.[10]

Polymer-based powders are categorized as either pristine or composite-type. The latter refers to a multiphase material, namely, a polymer into which reinforcing additives have been integrated. Pristine and composite-type powders are further classified according to their degree of crystallinity. The bulk of today's commercially-available SLS powders comprises pristine, semi-crystalline polymers, the most popular of which is Polyamide 12 (PA12), representing 90% of the total industrial consumption.[1] The remaining 10% comprises relatives of PA12 (including PA11- Polyamide 11 and Nylon 6- PA6), Polyether Ether Ketone (PEEK), thermoplastic elastomers and polyurethanes (TPEs and TPUs, respectively).[1] Relative to pristine polymers, composites have yet to break into the market.

Polymer Processability

Whether a given polymer powder is SLS-processable depends on the synergy between select intrinsic and extrinsic properties. Intrinsic properties, which are dictated by molecular structure, include optical, rheological, and thermal behavior.[11]

- Optical behavior: The polymer must be capable of absorbing the energy emitted by the SLS laser. If its absorption capacity is not within the wavelength range of the laser, fusion will not occur.
- Rheological behavior: Melt viscosity must be low in order to facilitate coalescence of the particles during sintering. Surface tension must also be low so that the powder bed is appropriately "wet out" by the fusing particles. The topography of each layer will be uneven if either of these requirements are not met, leading to imperfections in the sintered part.
- Thermal behavior: The temperature difference between the melting and crystallization points of the polymer, known as the sintering window, must be sufficiently wide. During processing, the temperature of the powder bed (T_B) is held within this range to expedite coalescence of the surface particles upon exposure to the laser. Furthermore, proper adhesion of the surface and previously-sintered layers is facilitated, as at T_B the latter have not yet cooled enough to crystallize and can still bond intramolecularly. If the sintering window is too narrow, premature crystallization may occur and cause curling within the sintered layers. Curling ultimately induces distortion and decreased resolution in the sintered part.

The extrinsic properties needed for a polymer to be SLS-processable concern the morphology of the particles and their distribution within the powder.

- Particle morphology: Particles should be spherical to promote free-flowing behavior. This behavior enables the particles to distribute homogeneously across the powder bed. A sintering layer that is not continuous implies a reduction in the powder density of that layer, which can deleteriously affect the mechanical properties of the part.
- Particle distribution: The ideal particle size distribution (PSD) should fall between 20 µm and 80 µm. The PSD should be relatively uniform, both in terms of volume and number of particles. If the number of small, very fine particles goes undetected- which is often the case with traditional PSD measurement techniques- the powder will not exhibit free-flowing behavior due to the enhanced intermolecular interactions between particles of smaller size.

Processing Parameters

Processing parameters are equally as important as material properties and must be adjusted to accommodate a given powder.

- Powder bed temperature: The temperature of the bed must fall within the aforementioned laser sintering window to facilitate melting and prevent premature crystallization.
- Layer thickness: The thickness of each sintered layer should be selected depending on the desired level of surface resolution within the final part. Thicker layers can lead to reduced surface finish due to the "stair step" effect.
- Laser power: The laser power must be optimized to ensure enough heat is supplied to the surface particles to induce fusion.
- Laser scan speed: The scan speed should be adjusted depending on the laser power. Typically, the smoothness of the sintering layer surface will decrease with increasing scan speed if the laser power is held constant.
- Laser energy density: Defined as "the amount of energy input per unit area," the energy density is directly proportional to the laser power and inversely proportional to the scan speed. All three parameters must be collectively tuned in accordance with the properties of the powder.
- Hatch distance: The amount of beam overlap between adjacent hatch lines, known as the hatch distance, heavily influences energy density and thus the mechanical properties of the part. The smaller the hatch distance, the higher the energy density and the potential for curling. Conversely, an increase in hatch distance may induce porosity within the part due to a lack of adequate overlap between sintered hatch lines.[12]

RESEARCH AND DEVELOPMENT

In the past decade, research efforts concerning SLS materials have focused on composite formulation and the use of additives to enhance the properties of printed parts. Espera, A.H. et al. investigated the mechanical and thermal properties of sintered parts produced using PA12 filled with various amounts of carbon black (CB). CB has been used extensively in manufacturing and its strength properties are well-known.[13] Commercially-available PA12 powder was blended with CB at concentrations of 0, 1.5, 3, 5, and 10% by weight. The resulting mixtures were then used to print parts via SLS. Mechanical properties were evaluated in terms of tensile and compressive strength. Relative to the control (pristine PA12), the 1.5% CB-PA12 composite exhibited a 200% improvement in tensile strength (Figure 2a) and a 400% increase in compressive strength (Figure 2b).[14]

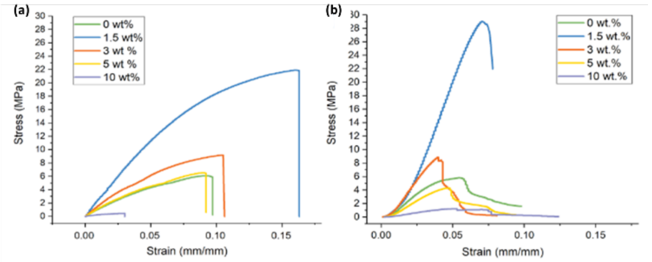


Figure 2. (a) Tensile strength data of composites with increasing CB loading. (b) Compressive strength test data of composites with increasing CB loading.[14]

The thermal stability of the CB-PA12 composites was assessed via thermogravimetric analysis (TGA). All the composites showed an increase in degradation temperature, T_{Max}; this is likely the result of CB's naturally-high T_{Max}, but nevertheless suggests an improvement in the thermal stability of the combined materials compared to the control (Figure 3a). Further analysis showed a decrease in the maximum rate of decomposition for the 1.5% and 3% CB-PA12 composites exclusively (Figure 3b). This phenomenon could be caused by the presence of combustion-inhibiting CB layers that were absent in the composites of higher CB concentration due to weaker adhesion between the filler particles and the polymer matrix.

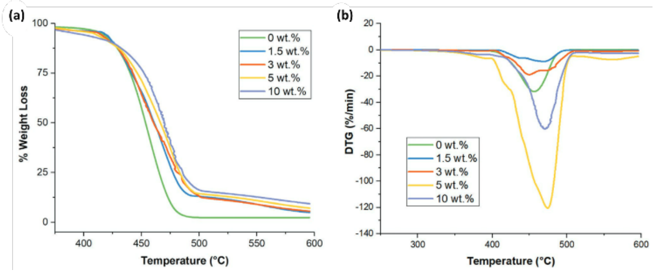
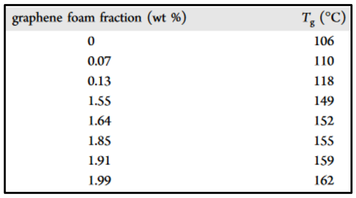


Figure 3. (a) Percent weight loss as a function of increasing temperature for CB-PA12 composites. (b) Decomposition rate as a function of increasing temperature for CB-PA12 composites.[14]

Another carbon allotrope considered for SLS composites is 3D graphene foam. 3D graphene was developed as an alternative to its famous cousin, 2D graphene. 2D graphene possesses excellent thermal, mechanical, and electrical properties but tends to agglomerate easily due to its planar structure and concomitant intermolecular interactions. The bulkier structure of 3D graphene is more conducive to resin infiltration and does not require dispersion techniques to achieve a uniform distribution within a polymer matrix. Furthermore, 3D graphene retains the desirable properties of 2D graphene despite their structural differences.[15] In 2017, Embrey, L. et al. compared the thermal and mechanical properties of epoxy composites containing 3D graphene foam to those of the pristine resin. Although the study used parts produced by dip-coating and mold-casting techniques, results could be applicable to SLS as well.

The thermal behavior of the composites was evaluated by means of differential scanning calorimetry (DSC) and revealed that the epoxy composites exhibited a significant increase in thermal stability. A 1.99 wt% addition of 3D graphene caused a 56°C increase in glass transition temperature (T_g) relative to the pristine epoxy. This could be due to a decrease in chain mobility brought on by excellent interactions between the filler and the epoxy matrix. T_g values increased with increasing 3D graphene content, as summarized in Table 1.

Table 1. Glass transition temperatures of 3D graphene foam epoxy composites.[15]



graphene foam fraction (wt %)	T_g (°C)
0	106
0.07	110
0.13	118
1.55	149
1.64	152
1.85	155
1.91	159
1.99	162

With regard to mechanical properties, an addition of 0.13 wt% 3D graphene increased ultimate tensile strength (UTS) of the mold-casted composite by 12% (Figure 4a). Flexural properties were also improved; a 0.6 wt% filler addition generated a 10% increase in fracture-resistance as measured by three-point bending test (Figure 4b).

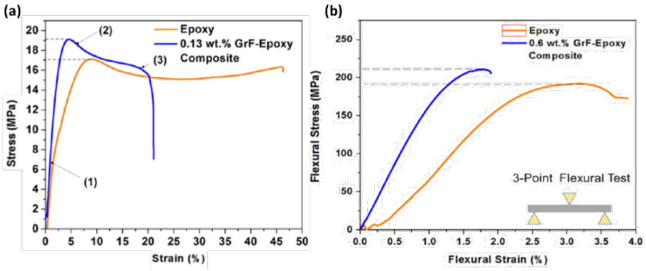


Figure 4. (a) Tensile stress-strain curve for pristine epoxy and mold-casted 3D graphene foam-epoxy composite. (b) Flexural stress-strain curve illustrating the improved strength of the composite relative to pristine epoxy.[15]

Finally, the group found that damping potential increased with increasing filler content. An addition of 1.99 wt% 3D graphene improved damping by an impressive 140% (Figure 5).

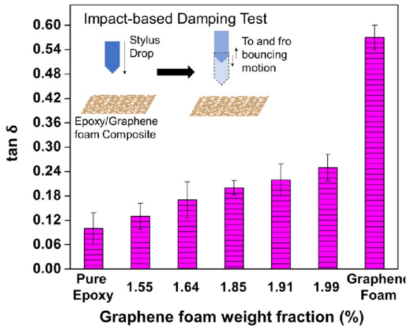


Figure 5. Loss tangent values for dip-coated 3D graphene foam-epoxy composites as a function of graphene foam weight fraction.[15]

Carbon nanotubes (CNTs) are yet another type of carbon-based filler that are of particular interest to the academic and industrial communities because of their exceptional strength and thermal properties. CNTs are classified as nanofillers, a group of fillers characterized by having at least one dimension in the nanoscale range.[16] Due to their high surface-to-volume ratio, CNTs can heavily influence the macroscopic properties of composites even in low concentrations. Bai, J. et alt. evaluated the mechanical behavior of sintered parts produced using a CNT-PA12 nanocomposite having only 0.1 wt% CNT. Parts were sintered using different laser powers to further understand the relationship between mechanical properties and laser power. Findings indicated that, regardless of laser power, both the flexural modulus and strength of the CNT-PA12 nanocomposite increased relative to the control, showing maximum improvements of 13.0% (Figure 6a) and 10.9% (Figure 6b), respectively.

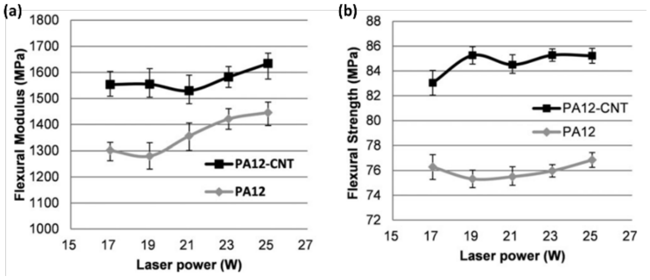


Figure 6. (a) Flexural modulus of PA12 and the CNT-PA12 composite with increasing laser power. (b) Flexural strength of PA12 and the CNT-PA12 composite with increasing laser power.[17]

The CNT-PA12 composite exhibited a consistent increase in toughness as well, most notably at a laser power of 25W, where impact strength improved 123.95% (Figure 7).[17]

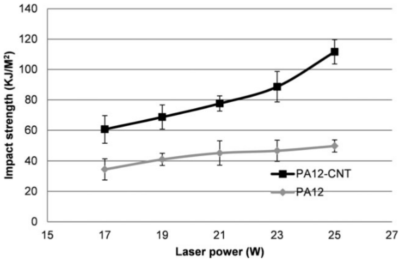


Figure 7. Impact strength with increasing laser power for pristine PA12 and the CNT-PA12 composite.[17]

Finally, the tensile properties of the CNT-PA12 composite were also enhanced, again regardless of laser power. The largest improvement in Young's Modulus (54%) was measured at a laser power of 19W (Figure 8a), whereas that of the UTS occurred at 25W, with an increase of 6.2% (Figure 8b).

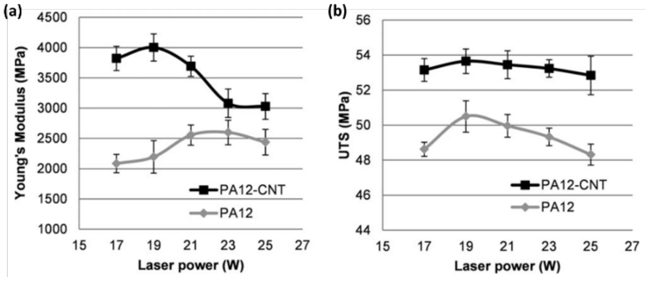


Figure 8. (a) Young's modulus of PA12 and the CNT-PA12 composite with increasing laser power. (b) UTS of PA12 and the CNT-PA12 composite with increasing laser power.[17]

SUMMARY AND OUTLOOK

AM is expected to play a significant role in the next industrial revolution, with SLS being its most adaptable technique.[1] SLS allows for the recycling of unused powders, the processing of a wide variety of materials, and freedom of design. Unfortunately, the portfolio of commercially-available SLS polymers is limited, whereas the breadth of formulations applicable to conventional manufacturing methods like injection molding and extrusion is extensive. Furthermore, parts produced via SLS do not consistently meet targeted performance requirements, a problem that can most easily be solved through material modification or reinforcement. Until the number of SLS polymers brought to market is expanded to include part-enhancing composites, the widespread adoption of SLS will continue to delay.

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