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Characterization of PA 12 Matrix Composites Produced by Selective Laser Sintering Method

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Abstract: The Selective Laser Sintering (SLS) method is a promising additive manufacturing (AM) technique for the production of thermoplastic polymers and polymer composite materials. Polyamide 12 (PA 12) is the most commonly used matrix material for the SLS AM method. Various additives are made to the polymer matrix to provide the desired physical, mechanical and tribological properties. In this study, composites with PA 12 matrix were produced by SLS method with 20% hollow ceramic microsphere (W100) reinforcement. Before production, PA 12 and ceramic additives were mixed by dry mixing method with a rotary tumbler. Then, thermal analysis (Differential Scanning Microscopy (DSC) and Thermogravimetric Analysis (TGA)) was performed to characterize the thermal properties of the powder mixture. Production parameters are one of the most crucial factors that affect SLS production. Composite samples and virgin PA 12 were produced with various SLS production parameters such as laser energy, scanning speed and hatch distance, and the effect of energy values on physical and mechanical properties were investigated. The samples underwent impact tests to determine their mechanical properties, and the fracture surfaces were subsequently analyzed.

Keywords: PA 12 composite, selective laser sintering (SLS), mechanical properties, ceramic additives.

Seçici Lazer Sinterleme Yöntemiyle Üretilen PA 12 Matrisli Kompozitlerin Karakterizasyonu

Özet: Seçici Lazer Sinterleme (SLS) yöntemi, termoplastik polimerlerin ve polimer kompozit malzemelerin üretimi için umut verici bir eklemeli üretim (AM) tekniğidir. Poliamid 12 (PA 12), SLS AM yöntemi için en yaygın kullanılan matris malzemesidir. İstenilen fiziksel, mekanik ve tribolojik özellikleri sağlamak için polimer matrise çeşitli katkılar yapılmaktadır. Bu çalışmada, PA 12 matrisli kompozitler %20 içi boş seramik mikroküre (W100) takviyesi ile SLS yöntemi ile üretilmiştir. Üretim öncesinde PA 12 ve seramik katkılar kuru karıştırma yöntemi ile döner tamburda karıştırılmıştır. Ardından, toz karışımının termal özelliklerini karakterize etmek için termal analizler (Diferansiyel Tarama Mikroskopisi (DSC) ve Termogravimetrik Analiz (TGA)) gerçekleştirilmiştir. Üretim parametreleri SLS üretimini etkileyen en önemli faktörlerden biridir. Kompozit numuneler ve sinterlenmemiş PA 12, lazer enerjisi, tarama hızı ve tarama mesafesi gibi çeşitli SLS üretim parametreleri ile üretilmiş ve enerji değerlerinin fiziksel ve mekanik özellikler üzerindeki etkisi araştırılmıştır. Numuneler mekanik özelliklerini belirlemek için darbe testlerine tabi tutulmuş ve ardından kırılma yüzeyleri analiz edilmiştir.

Anahtar Kelimeler: PA12 kompozit, seçici lazer sinterleme (SLS), mekanik özellikler, seramik katkı.

Article

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1.Introduction

Additive manufacturing (AM) is a manufacturing process that embodies the idea of additive design by layering material with computer-aided design (CAD). The terms 3D printing, direct digital manufacturing, freeform manufacturing, rapid prototyping, additive manufacturing, and additive layer manufacturing are also used to describe the AM process (Özbay & Serhatlı, 2022). Based on machine size, nozzle dimensions, nozzle speed, and workspace dimensions, AM processes and machines can be categorized. According to the material's functional structure, AM can be divided into many different categories (Mohanavel et al., 2021). While the patterning energy, the way of creating primitive geometry, the kind of materials utilized, and the support process are other possible classification techniques. On the other hand, AM procedures can be broadly categorized and summed up based on the kind of material that is employed (Abdulhameed et al., 2019). Based on the kind of additive manufacturing types, Figure 1 presents an overview of the current AM techniques.

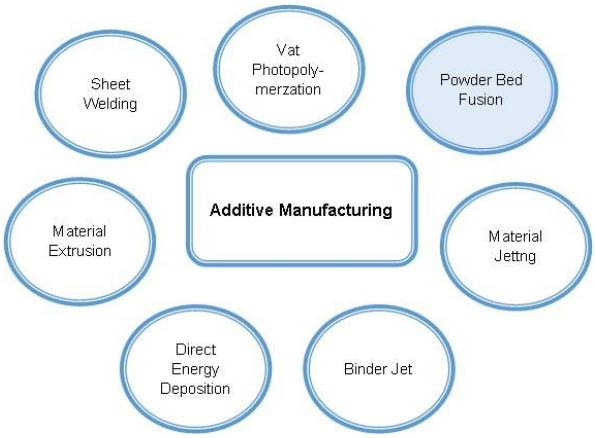

Figure 1. Classification of AM processes.
Şekil 1. AM işlemlerinin sınıflandırılması.

The purpose of powder bed methods is to consolidate material to create 3D printed parts layer by layer using fine particles of various types (metallic, ceramic, or polymeric) as feedstock. Depending on the technique, these methods are powered by different sources. These AM methods enable the creation of extremely intricate structures by layering the powder particles together and fusing them together using a heat source to solidify the feedstock (Godec et al., 2022). The powder bed fusion (PBF) process using direct heating is selective laser sintering (SLS) or selective laser beam melting (SLBM) (Espera et al., 2019). Since SLS was the first technology to be commercialized under this AM category, it has grown to be the most well-liked PBF procedure (Attar, 2011). Carl Deckard created selective laser sintering in 1989 (Deckard, 1988). The University of Texas owns the patent. Metal materials were used for additive manufacturing by Manriquez-Frayre and Brouell in 1990 (Harris L. Marcus et al., 1993). SLS is an additive manufacturing technique used to create solid objects by selectively targeting a bed of powdered metal, thermoset, or thermoplastic to a heating source, such as carbon dioxide (CO_2), an Nd-YAG laser, fiber, or diode, thereby melting the powder (Gu, 2015). A hybrid SLS method was developed by Wudy and Drummer that employs mixed reactive liquids of thermoset resin and thermoplastics. The traditional materials utilized in a standard SLS system are thermoplastics like polyamide 12 (PA 12), polyamide 11 (PA 11), polypropylene, and thermoplastic elastomers (Wudy & Drummer, 2019). Before sintering, the chamber is typically heated to a temperature just below the melting point of the powder material. The powder ingredients are partially melted by an intense laser beam that is focused into the print region and moves in an X-Y direction. Materials that have partially melted combine to form an object layer (Sachs, 1990). As the printing area piston moves down and the powder chamber piston moves up, the levelling drum will smoothly apply a fresh layer of powder onto the printing surface. After the printing process is fully executed within the chamber, printing will come to a close. To achieve the desired shape, extra powder is shaken off (Kerns, 2015). The strength and speed of the laser, the size of the powder material's particles, and the layer thickness all affect the SLS print quality (Gibson, & Shi, 1997). The majority of the time, printed support structures are used to hold 3D models with projecting layers (features that are more than 45 degrees from the vertical). SLS eliminates the requirement for structural support because the powder secures the manufactured product. Thermoplastic polymers, including polyurethane (TPU), polycaprolactone (PCL), and polyamide (PA), are the most often used materials in SLS. Ceramic, glass, aluminum or fiber elements can be added to these thermoplastics to suit specific purposes. Industrial-grade SLS equipment also utilizes metals and ceramics (Kim, & Oh, 2008). Particle type additives can be used to enhance the mechanical properties of SLS parts, especially when high hardness and toughness are necessary for industrial applications. By adding reinforcing materials such as platelets, whiskers, fibers or particles made of ceramics, metals or polymers, the stiffness and toughness of polymers can be improved. Polymer composites, which are frequently utilized in engineering applications, are composite materials created by incorporating such secondary components into the polymer matrix. Due to their greatly enhanced mechanical, physical, thermal, and electrical qualities with little filler content, polymer composites are becoming more popular (Monfared, 2021; Han, 2022). In the literature, Mousa looked at the mechanical characteristics of composites with glass beads added to PA 12 structures. The testing results proved that the addition of glass beads boosted the composite sections' tensile strength and elastic modulus while decreasing their impact strength. To a certain degree when the percentage of glass beads is increased, particularly when it reaches 10%. The impact strength significantly decreased with loading up to 20 weight percent (Mousa, 2014). Chunze and colleagues utilized nano silica as a nanofiller to reinforce polyamide 12 in the SLS process. Using the dissolution-precipitation process, 3% by weight of nano silica was combined with PA 12. A composite powder was created using the dissolution precipitation method. The study found that the SLS printed samples exhibited notable enhancement in tensile strength, tensile modulus, and impact strength by 20.9%, 39.4%, and 9.54% respectively, as compared to unfilled PA 12 (Chunze, 2019). Chung and Das used SLS to manufacture Nylon 11/silica nanocomposites with a functional gradient. They created powder mixtures of Nylon 11 and silica nanoparticles (0-10% by volume) using a spinning drum. The mechanical properties of the nanocomposites did not follow a linear pattern when the filler volume percentage changed (Chung, & Das, 2008).

In this study, PA 12 material was used as a polymer matrix. For the improvement of the physical and mechanical features of PA 12, a hollow ceramic microsphere was added as an additive. A ceramic contribution of 20 percent by weight will be made, which will form the basis of the current research. As a result of the study, is aimed at reducing the density of the composite structure and obtaining lightness. Test specimens for the Charpy test were produced and tested with open notches to reduce possible errors caused by notching mechanical test specimens.

2. Materials and Methods

2.1 Materials

As a polymer matrix, PA 12 (PA2200, EOS GmbH) was the matrix material used in this work. Hollow Ceramic Microsphere (W100) from ELMINAS Company (ELMINAS-SPHERES® THERMO – W) was utilized as an additive. The PA 12 and W100 powder's average grain sizes are 60 µm and 100 µm, respectively. In this work, different amounts of W100 reinforced PA 12 were produced using the SLS process to decrease the density of the final polymer composite structures while retaining their mechanical properties. Figure 2 shows the SEM images of the ceramic solid and polymer powder used in the study.

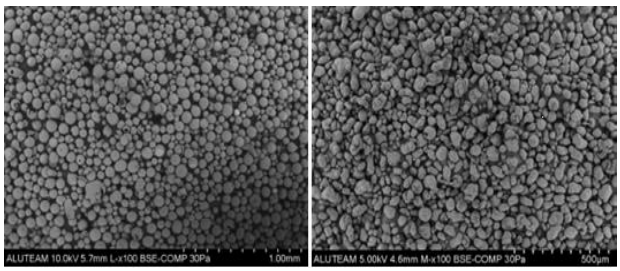

Figure 2. SEM Images of Hollow Ceramic Microsphere Powder (left) and PA12 powder (right).
Şekil 2. İçi boş seramik küre tozu ve PA12 tozunun SEM görüntüleri.

2.2 Processing techniques

It is possible to fabricate composites of PA 12/W100 using SLS with a layer height of 100 microns. A CO_2 laser with a maximum laser output of 30 W is equipped with the EOS P 110. A composite was created by mixing polymer particles in a rotating tumbler. To achieve 20 wt. %, the reinforcement powders (W100 particles from ELMINAS) and matrix (PA 12 / PA 2200 from EOS GmbH) were properly combined. PA 12 polymer reinforced with W100 was created using SLS at a variety of energy densities between 0.0300 and 0.0500 J/mm^2. The hatch distances of samples 1 and 2 are 0.15 and 0.25 mm, respectively. For samples 3 and 4, 0.15 and 0.25 were chosen, respectively. The laser power of each parameter was kept the same at 21 W. The ideal temperatures for manufacturing were 173 °C in the process chamber and 153 °C in the removal chamber. PA 12 composite's optimal processing temperature was found to be 173 °C. Table 1 displays the processing variables. The calculation of Energy Density (ED) is shown in the formula below (Eq. (1)). Density of energy (J/mm^2), laser power (W), laser scan speed (mm/s), and hatch distance (mm), are represented by the letters ED, P, v, and h. The ED unit will be J/mm^3 when the layer thickness is taken into account in the ED computation.

$$ED = \frac{P}{V*h} \quad (1)$$

Table 1. Processing parameters of SLS manufacturing.
Tablo 1. SLS üretiminin işlem parametreleri.

Sample Number	Laser power (W)	Scan speed (mm/s)	Hatch distance (mm)	Energy (J/mm^2)
1	21	4665	0.15	0.0300
2	21	2800	0.25	0.0300
3	21	2800	0.15	0.0500
4	21	1680	0.25	0.0500

2.2.1 Thermal analysis

DSC and TGA measurements were made on a TA Instruments-SDT 650 thermal analyzer. The sintering window range, crystallization temperatures, and melting temperatures were determined using DSC analysis. By calculating the sintering window area, DSC graphs were used to estimate the ideal laser processing parameters and processing temperature range. In this investigation, PA 12 composites were subjected to increased energy densities and temperatures.

2.2.2. Microstructural, Physical and Mechanical Analyses

Density measurements were performed on sintered samples. An analytical balance with a density kit, the Precisa XB 220A, was used to measure the densities of sintered materials. Moreover, the porosity content of the produced was calculated with the rule of mixture by using theoretical and experimental density values. On the other hand, the charpy impact tests were performed by Devotrans CD-1 impact test equipment. The powder structure before the SLS process was analyzed by Hitachi SU3500 T2 Scanning Electron Microscope (SEM). In addition, the SEM device was used to examine and analyze the microstructure images of the composite samples after the impact test.

3. Results and Discussion

3.1. Thermal analysis

Using DSC analysis (DIN EN ISO 11,357 ((ISO 11357-1:2016, 03.11.)), the determination of sintering windows was carried out to ascertain the melting and crystallization temperatures of PA 12 and its various combinations. Table 2 demonstrates the temperatures at which PA 12, and W100 reinforced PA 12 mixes melt and crystallize, as well as the melting and crystallization beginning points. DSC analysis was applied to both unprocessed powder and powder mixture separately. According to the findings of the DSC tests, it can be concluded that the adjunct of W100 and the growing concentration of W100 in the PA 12 polymer matrix raise the crystallization temperature. While the crystallization temperature is reached at higher temperatures, the additive serves as the nucleus. As a result, larger energy density values and processing temperatures will be required (Özbay et al., 2022). Additive material causes a discernible increase in crystallization temperature (Tc) and melting temperature (Tm) onset values. In addition, the addition of W content results in a small decrease in Tc and Tm peak temperatures.

Table 2. Temperature values of PA 12 and PA 12-W100.
Tablo 2. PA 12 ve PA 12-W100 sıcaklık değerleri.

Sample Number	T_m onset	T_c onset	T_m peak	T_c peak
PA 12	177.09	139.56	187.59	139.56
PA 12-W100	179.29	144.09	186.88	137.67

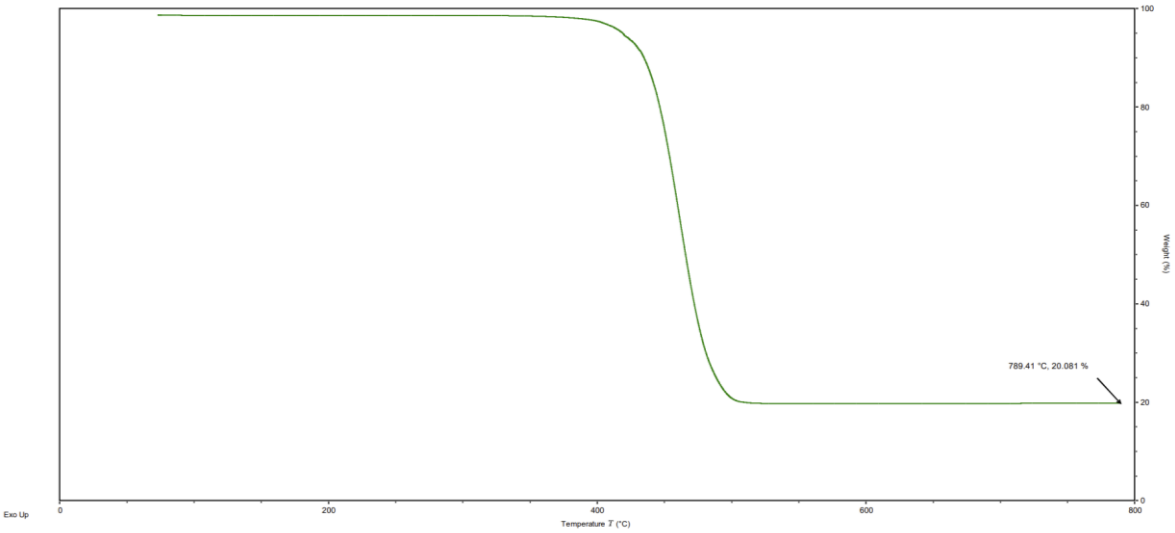

Figure 3. TGA analysis result of the powder mixture.
Şekil 3. Toz karışımının TGA analizi sonucu.

TGA analysis has been done by the following step of 20°C/min, from room temperature to 800 °C. According to the analysis result, 20% residue has been achieved as the additive amount in the powder mixture which points to the appropriate prepared mixture. TGA analysis result of the powder mixture can be seen in Fig.3.

3.2 Microstructural, physical, and mechanical test results

The density and porosity of the produced samples can be seen in Fig. 4. The bulk density values of the PA 12 and W100 were determined as 0.99 g/cm^3 and 0.80 g/cm^3, respectively. The experimental density of the samples was determined by Archimedes principle, and the values were given in Fig. 4. Moreover, the porosity content of the samples was calculated. As mentioned earlier, it was seen that the microstructure of the composites was similar in terms of porosity content. However, it was clearly seen that the porosity content of the samples was decreasing with increasing energy density and decreasing scan speed. By increasing the unit energy density and decreasing the scanning speed during composite production, the energy input into the system increased, and denser structures were formed with a higher melting tendency of the PA 12 matrix.

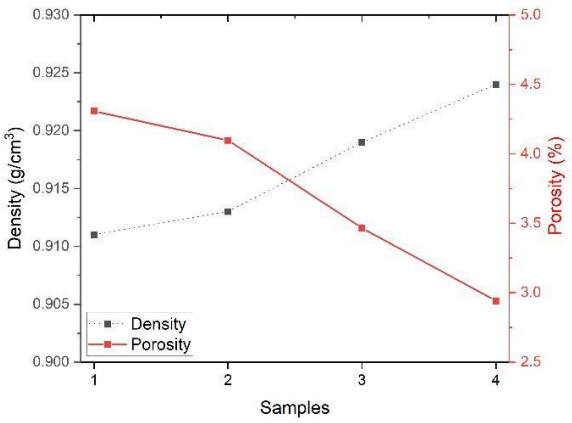

Figure 4. Experimental density and porosity content of the samples.
Şekil 4. Numunelerin deneysel yoğunluk ve porozite değerleri.

The microstructures of all produced samples show a homogenous distribution of the W100 ceramic particles in the PA 12 matrix, as shown in Fig. 5. The microstructure of the composites was similar, and it can be emphasized that matrix-reinforcement interaction provided between the PA 12 and W100 and the properties of the PA 12 were improved.

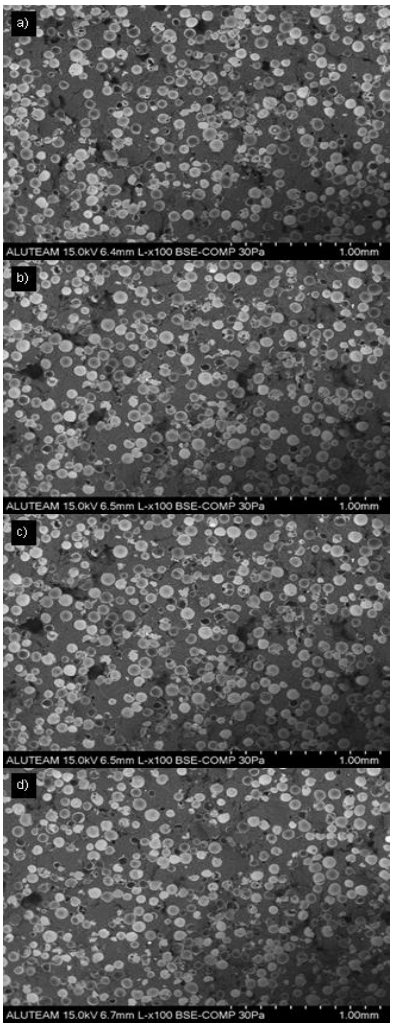

Figure 5. Microstructure of the samples a) Sample 1, b) Sample 2, c) Sample 3, d) Sample 4.
Şekil 5. Numunelerin mikroyapısı a) Numune 1, b) Numune 2, c) Numune 3, d) Numune 4.

The results of the composite samples' impact tests are presented in Fig. 6. The Charpy impact strength was found to be most affected by the energy density value. In samples 3 and 4, where the energy density value was 0.0500 J/mm^2, higher impact strength was obtained compared to samples 1 and 2. The impact strength value was determined to increase depending on the hatch distance and scan speed values. On the other hand, it was observed that the change in hatch distance and scan speed values has no significant effect on impact strength at lower energy density (0.0300 J/mm^2).

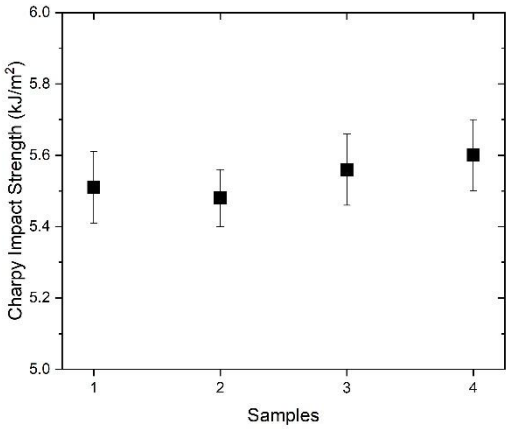

Figure 6. Charpy impact strength of the samples.
Şekil 6. Numunelerin Charpy darbe dayanımı.

4. Conclusion

In this study, PA 12 matrix 20% void ceramic microsphere (W100) reinforcement composites were produced with SLS with different hatch distance (0.15 mm - 0.25 mm) and energy (0.0300 J/mm^2 - 0.0500 J/mm^2) process parameters. Generally, composite production was achieved for all parameters. At lower energy density values, it was observed that changes in the values of parameters such as scan speed and hatch distance do not significantly affect impact strength values. However, the increase in energy density increased the melting tendency of the PA 12 matrix, resulting in increased impact strength and a denser structure. Increasing the energy density value caused an increase in the energy transferred to the material in the production of composite material by SLS method. Accordingly, the reinforcing element-matrix interaction was enhanced. Thus, the porosity in the structure was reduced, the density was increased and the impact strength was improved. Density and porosity values were also compatible with the phenomenon.

5. Acknowledgements

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6. Conflicts of Interest

The authors declare no conflict of interest.

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