

Study on the development of 3D printing materials based on blend of polyamide 6 and polyamide 11

Dinh The Dung^{1*}, Nguyen Tran Hung¹, Le Minh Tri²,
Le Huu Dat³, Nguyen Vu Giang³, Pham Thi Thanh Nhan⁴

¹Institute of Chemistry and Materials, Academy of Military Science and Technology, 17 Hoang Sam, Cau Giay, Hanoi, Vietnam;

²Academy of Military Science and Technology, 17 Hoang Sam, Cau Giay, Hanoi, Vietnam;

³Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam;

⁴Vietnam–Hungary Industrial University, 54 Vu Trong Phung, Thanh Xuan, Hanoi, Vietnam.

*Email: gnudktvn@gmail.com

Received 11 Feb. 2025; Revised 27 Mar. 2025; Accepted 04 Apr. 2025; Published 15 Apr. 2025.

DOI: <https://doi.org/10.54939/1859-1043.j.mst.102.2025.101-108>

ABSTRACT

3D printed CF/PA6+PA11 filaments are created from a blend of BASF's polyamide 6 (PA6), Arkema's polyamide 11 (PA11), and carbon fibers from Toray (Japan). This study focuses on evaluating the blend ratios of PA6, PA11, and the composite ratios of the blend with carbon fibers in the production of 3D printed filaments. Key technical parameters such as tensile strength, flexural strength, and impact strength were measured to assess mechanical performance under filament fabrication conditions. The study determined that a blend ratio of 70:30 for PA6:PA11 provides the best compatibility. Based on the PA6 and PA11 blend, the 3D printed CF/PA6-PA11 filament achieved suitable mechanical properties with component ratios of PA6, PA11, short carbon fibers (≤ 0.3 mm), and long carbon fibers (0.3 mm – 1 mm) at 49%, 21%, 20%, and 10%, respectively.

Keywords: 3D printing; Composite material; Polyamide 6; Carbon fiber.

1. INTRODUCTION

Nowadays, 3D printing technology is considered a modern manufacturing method that is gradually replacing traditional material production techniques. Among the various methods, Fused Deposition Modeling (FDM) is the most popular and widely used. This method allows the fabrication of materials combined with different reinforcement agents to enhance the strength of printed components. Many products manufactured using this technology exhibit higher durability compared to metal-based materials [1].

Presently, the applications of this method are expanding across numerous fields, ranging from education [2], art [3], and healthcare [4-6], to advanced technology sectors such as the automotive industry [7, 8], aerospace [3, 9-11], and defense weaponry [11-12]. The materials commonly used in FDM 3D printing are recyclable thermoplastics such as ABS, PLA, and PE. For products requiring high technical performance, engineering-grade plastics like PA6 or PEEK can be used.

In the authors' previous research [13], 3D-printed composite filaments were successfully produced using a blend of polyamide 6 (PA6) and carbon fibers. These filaments were applied in FDM 3D printing to manufacture components with high mechanical strength. However, a limitation identified in the CF/PA6 material was its insufficient impact strength, making it unsuitable for certain applications requiring precise mechanical components.

Therefore, this study focuses on enhancing the impact strength to improve the mechanical performance and applicability of the material for components subjected to high-impact loads. To address this issue, the authors utilized PA11 blended with PA6. PA11, known as an engineering polyamide, offers several advantages, such as high hardness, excellent deformation resistance, and

superior impact resistance. Similar to other polyamides, PA11 is also chemically resistant to acids and bases, easy to process, and recyclable.

PA11 is commonly used in products that require mechanical load-bearing capacity, such as automotive interior components and continuously moving parts [14]. This study aims to determine the optimal blend ratio of PA6 and PA11, along with the appropriate proportions of each component, to produce 3D-printable filaments. The study will further fabricate and experimentally evaluate the mechanical performance of the resulting products.

2. EXPERIMENT

2.1. Materials

- Pristine PA6 resin from BASF (Germany) has a melting temperature of 220 °C (± 2 °C), a density of 1.12 g/cm³ (± 0.02 g/cm³), and a decomposition temperature of 438 °C (± 5 °C);
- PA11 resin from Arkema (France) has a melting temperature of 190 °C (± 2 °C), a density of 1.05 g/cm³ (± 0.02 g/cm³), and a decomposition temperature of 248 °C (± 5 °C);
- Carbon fibers from Toray (Japan) have a fiber diameter of 5 μ m, a density of 1.75 g/cm³ (± 0.03 g/cm³), and a carbon content exceeding 99%.

2.2. Fabrication of materials

Fabrication of PA6 and PA11 blend

Before use, PA6 and PA11 resins were dried at 80 °C for 8 hours to remove moisture.

The blend material was fabricated using the melt blending method. The PA6/PA11 mixtures (with weight ratios of PA6:PA11 at 80:20, 70:30, and 60:40) were accurately weighed and mechanically mixed. The samples were fed into a Haake Rheomix 610 internal mixer, ensuring a fill factor of 0.7 in the mixing chamber. The blend was processed at a temperature of 235 °C, a rotor speed of 50 rpm, and a mixing time of 5 minutes using the internal mixer Haake.

After mixing, the molten samples were removed and transferred to a TOKYOSEIKY hydraulic press to form flat sheets under a pressing temperature of 220 °C and a pressure of 20 MPa. The samples were cooled and stored in a desiccator before conducting material property evaluations.

Processing of carbon fibers

The carbon fibers were ground using a GM-800S1 grinder (Germany) and size-classified using a China 8411 vibrating sieve. The sieves had mesh sizes of 1 mm for long carbon fibers and 0.3 mm for short carbon fibers.

Fabrication of composite material based on PA6/PA11 blend and carbon fibers

Before use, PA6 and PA11 resins were dried at 80 °C for 8 hours to remove moisture.

The composite samples were prepared with the following weight ratios:

Sample	PA6 (%)	PA11 (%)	Short Carbon Fibers (%)	Long Carbon Fibers (%)
1	49	21	30	0
2	49	21	25	5
3	49	21	20	10
4	49	21	15	15

The above mixtures were processed using a twin-screw extruder. The extrudate was cooled and cut into pellets. The pellets were stored in vacuum-sealed bags to prevent moisture absorption.

Before filament extrusion, the pellets were dried at 80 °C for 4 hours to eliminate residual moisture. The dried pellets were then extruded and wound into filaments using a filament extrusion and winding device (figure 1). The parameters of the spinning process are as follows: a screw

Research

rotation speed of 12 rpm, three heating zones of the screw set at 210 °C, 220 °C, and 230 °C, respectively, and a fiber diameter of 1.75 ± 0.05 mm.

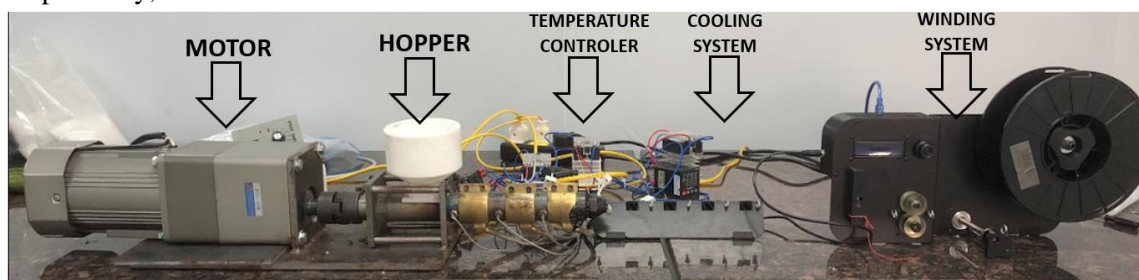


Figure 1. 3D filament manufacturing device.

Fabrication of materials using FDM 3D printing method

Printing Device: Creality Ender 3 S1 Pro

Parameters of printing processing:

No	Printing Mode	Parameter
1	Build plate temperature (°C)	110
2	Nozzle temperature (°C)	273
3	Printing speed (mm/s)	100
4	Infill density (%)	50
5	Infill pattern	Concentric
6	Number of shell layers	2
7	Layer Height (mm)	2

Printed Component: Six mechanical parts for the **shaft inspection machine** were fabricated as test samples (figure 2).

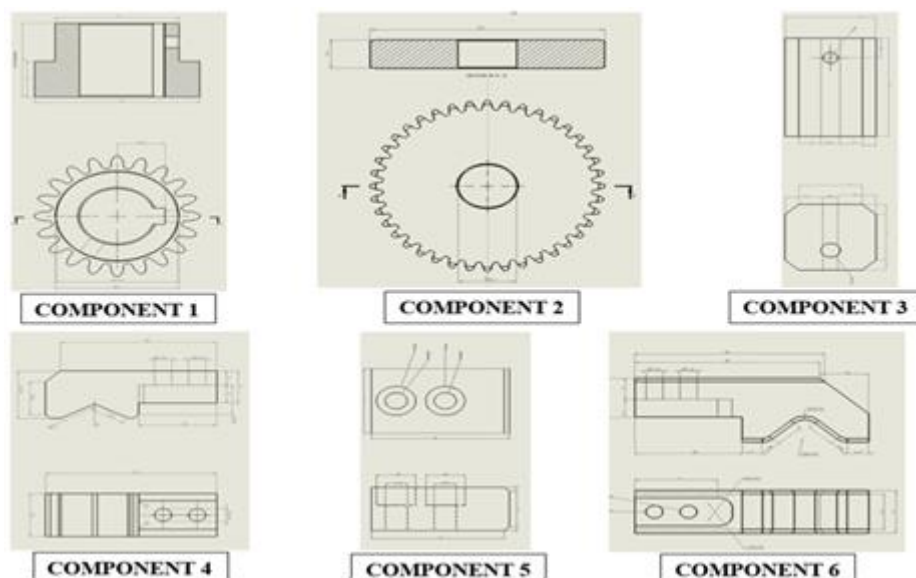


Figure 2. Prototype drawing.

2.3. Research methods

The fabrication of the PA6 and PA11 blend was carried out using a Haake Rheomix 610 internal mixer at the Institute of tropical engineering.

The processing of carbon fibers was performed using a GM-800S1 grinder (Germany) and a China 8411 vibrating sieve at the Institute of chemistry and materials.

The fabrication of composite material from the PA6/PA11 blend and carbon fibers was conducted using a LEISTRITZ twin-screw extruder (Germany) at the Polymer materials research center, Hanoi university of science and technology.

The fabrication of 3D printing filaments was conducted at the Institute of chemistry and materials.

The mechanical properties of the CF/PA6 3D printing filament were evaluated as follows:

- Tensile strength was measured using a Zwick Z2.5 testing machine (Germany) according to ASTM D638.
- Flexural strength was measured using a Shimadzu testing machine according to ASTM D790.
- Impact strength was determined using a TestResources impact tester according to ASTM D256-10.
- Heat deflection temperature (HDT) was measured using a Vicat tester according to ASTM D648 at the Institute of tropical engineering.

3. RESULTS AND DISCUSSION

3.1. Study on the properties of PA6 and PA11 blend

Based on previously published research [13], PA11 was used to enhance the impact strength of the material. PA11 is a high-performance engineering plastic, and its incorporation into the blend improves its elasticity, thereby increasing the impact strength. Both PA6 and PA11 are synthetic polymers belonging to the family of aliphatic polyamides. They have a main carbon backbone structure with amide (-CONH-) groups connecting each repeating unit. These amide groups form relatively strong hydrogen bonds between polymer chains, resulting in a semi-crystalline structure. Both PA6 and PA11 exhibit good chemical, thermal, and mechanical resistance due to this structure.

When blending the two polymers, phase compatibility plays a decisive role in determining the material's properties. If the phases are compatible, a homogeneous phase will be obtained. Conversely, phase separation will occur (figure 3).

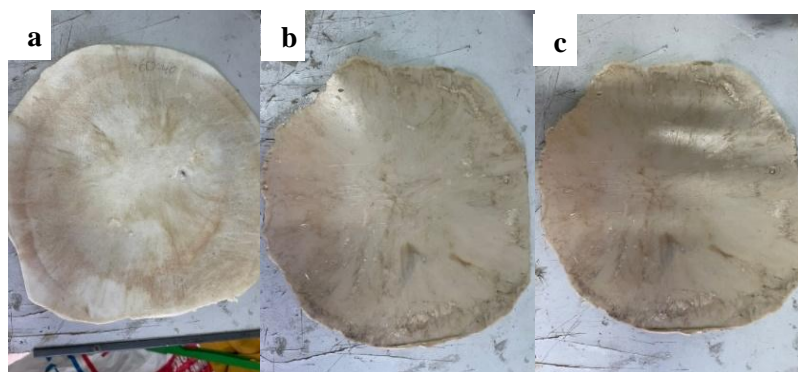


Figure 3. PA6/PA11 blend with the ratio: 60:40 (a), 70:30 (b) và 80:20 (c).

In the case of PA6/PA11, they are only compatible to a certain extent due to the differences in chain length. The data in the table shows the technical parameters of polyamide 6 (PA6) and the PA6/PA11 blend at various ratios (table 1):

- *Tensile Modulus*: PA6 has a tensile modulus of 396.6 MPa. When blended with 20% PA11, the tensile modulus increases to 500.7 MPa, surpassing that of PA6. However, when the PA11 content is increased to 30% and 40%, the tensile modulus decreases to 388.4 MPa and 353.7 MPa,

respectively. This indicates that the optimal ratio for improving the modulus of elasticity is a blend of 80% PA6 and 20% PA11. A higher PA11 content reduces the material's stiffness.

- *Tensile Strength and Elongation at Yield Point:* PA6 has a tensile strength of 56.6 MPa and an elongation of 34.7% at the yield point. When blended in a 80:20 PA6:PA11 ratio, no data is available for the yield point. However, at 70:30 and 60:40 ratios, tensile strength and elongation decrease to 42 MPa, 40.6 MPa and 31.5%, 27.3%, respectively. This suggests that increasing the PA11 content reduces the ductility of the blend compared to PA6.

- *Tensile Strength and Elongation at Break Point:* PA6 has a tensile strength of 52.3 MPa and an elongation of 93.1% at the break point. At a PA6:PA11 blend ratio of 80:20, the tensile strength drops to 38.6 MPa, but elongation increases to 94.3%. At 70:30 and 60:40 ratios, tensile strength increases to 55.3 MPa and 54.2 MPa, respectively, and elongation also increases compared to PA6. In general, increasing the PA11 content enhances the elongation and load-bearing capacity at the break point of the material compared to PA6.

- *Impact Strength:* Pure PA6 has an impact strength of only 97 J/m, whereas all PA6/PA11 blends do not break during impact testing according to ASTM D256. This demonstrates that blending PA6 with PA11 significantly improves the material's impact resistance compared to pure PA6.

Table 1. Material properties based on PA6 and PA11 blend.

Technical Parameter	Method	PA6	Blend (PA6 and PA11)		
			Ratio 80:20	Ratio 70:30	Ratio 60:40
Tensile Modulus, MPa	ASTM D638	396,6	500,7	388.4	353,7
Tensile Strength at Yield, MPa	ASTM D638	56,6	-	42,0	40,6
Elongation at Yield, %	ASTM D638	34,7	-	31,5	27,3
Tensile Strength at Break, MPa	ASTM D638	52,3	38,6	55,3	54,2
Elongation at Break, %	ASTM D638	93,1	94,3	159,5	170,3
Impact Strength, J/m	ASTM D256-10	97,0	No break	No break	No break

In summary, blending PA6 with PA11 at an optimal ratio of 70:30 or 60:40 improves properties such as load-bearing capacity, elongation at break, and especially impact strength compared to pure PA6. However, this also leads to a reduction in tensile strength at yield and tensile modulus when the PA11 content is too high. Therefore, to balance these properties, the authors chose a 70:30 PA6:PA11 blend as the base material for the 3D printing filament manufacturing process.

3.2. Study on the properties of composite material based on PA6/PA11 blend and carbon fibers

To further enhance the tensile modulus of the material compared to that reported in [13], in addition to the carbon fibers previously used, the long carbon fibers with a length of 0.3 - 1.0 mm were introduced. To balance the impact strength, tensile modulus, and elongation, the content of short and long fibers at the ratios presented in table 2 was investigated.

Based on the results in table 2, several trends can be observed as the ratio of long carbon fibers increases in the blend with short carbon fibers:

- Tensile modulus increases from 657 MPa (with 0% long fibers) to 3302 MPa (with 15% long fibers).
- Tensile strength at break increases from 63.2 MPa (with 0% long fibers) to 104.4 MPa (with 15% long fibers), an increase of nearly 65%.

- Flexural strength increases from 70.6 MPa (with 0% long fibers) to 118 MPa (with 15% long fibers), an increase of nearly 67%.
 - Flexural modulus increases from 2155 MPa (with 0% long fibers) to 4616 MPa (with 15% long fibers).
 - Heat deflection temperature (HDT) increases from 143 °C (with 0% long fibers) to 165 °C (with 15% long fibers).
 - Impact strength increases from 211.6 J/m (with 0% long fibers) to 510.4 J/m (with 15% long fibers).
- However, some properties tend to decrease as the ratio of long fibers increases:
- Tensile strength at yield decreases from 66.7 MPa (with 0% long fibers) to 56.1 MPa (with 10% long fibers).
 - Elongation at yield decreases from 21.5% (with 0% long fibers) to 30.1% (with 10% long fibers).
 - Elongation at break decreases sharply from 145.2% (with 0% long fibers) to 14.4% (with 15% long fibers).

Table 2. Properties of the PA6/PA11 blend (70:30 blend ratio) and carbon fibers at different ratios.

Technical Parameter	Method	Composite material with different ratios of short carbon fibers: long carbon fibers (%)			
		30:0	25:5	20:10	15:15
Tensile Modulus, MPa	ASTM D638	657	1414	1805	3302
Tensile Strength at Yield, MPa	ASTM D638	66,7	58,9	56,1	-
Elongation at Yield, %	ASTM D638	21,5	25,4	30,1	-
Tensile Strength at Break, MPa	ASTM D638	63,2	67,1	69,7	104,4
Elongation at Break, %	ASTM D638	145,2	101,2	94,3	14,4
Flexural Strength, MPa	ASTM D790	70,6	94,3	101,9	118
Flexural Modulus, MPa	ASTM D790	2155	2915	3308	4616
Heat Deflection Temperature (HDT), °C		143	154	161	165
Impact Strength, J/m	ASTM D256-10	211,6	324,4	361,9	510,4

As the ratio of long carbon fibers increases, the mechanical properties of the composite material significantly improve, including tensile strength, flexural strength, elastic modulus, and impact strength. However, long carbon fibers possess very high mechanical properties, such as high stiffness and tensile strength, but are also quite brittle. As the carbon fiber content increases in the composite, the material becomes stiffer and less ductile. This leads to a reduction in the material's ability to deform before reaching the yielding or fracture point. The research results indicate that a carbon fiber content of 20% short fibers and 10% long fibers in the composite material provides the optimal performance.

3.3. Evaluation of the printed test components

For the application of the fabricated material, YMT Co., Ltd., the entity using the components made with the 3D composite printing method from the project's products, provided the following specific evaluations:

- For the mechanical properties and material durability: hardness, wear resistance, impact resistance, and chemical resistance all meet the requirements for replacing mechanical components used in the **shaft inspection machine**;

- For the dimensions of the 3D printed components: after measuring the printed dimensions against the drawings, it was found that the printed components meet class 1 standards, making them suitable for use in mechanical devices.

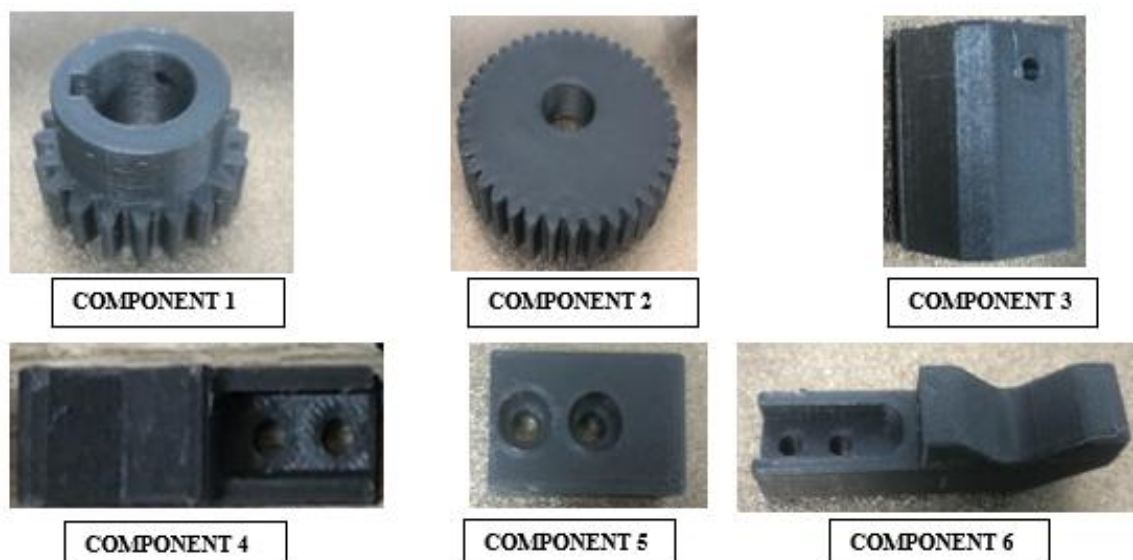


Figure 4. Details of the *shaft inspection machine* equipment printed by composite material based on PA6/PA11 blend.

4. CONCLUSIONS

For the PA6 and PA11 blending process, the optimal blend ratio of these two resins is 70% PA6 and 30% PA11, providing the best compatibility based on technical parameters.

For 3D printing filaments used in FDM technology to print mechanical components requiring high impact strength, the appropriate component mass ratio of PA6, PA11, short carbon fibers, and long carbon fibers in the filament is 49%, 21%, 20%, and 10%, respectively.

Acknowledgements: The authors would like to thank the funding support from the Military Science and Technology Institute, Project No. 02/2024/HDKHCN-HHVL.

REFERENCES

- [1]. <https://markforged.com/resources/blog/replacing-aluminum-parts-with-3d-printed-carbon-fiber>
- [2]. Dhinakaran, V., et al., "A review on recent advancements in fused deposition modeling", *Materials today: proceedings*, **27**, p. 752-756, (2020).
- [3]. Singh, R. and H.K. Garg, "Fused deposition modeling—a state of art review and future applications", Reference Module in Materials Science and Materials Engineering, p. 1-20, (2016).
- [4]. Winarso, R., et al., "Application of fused deposition modeling (FDM) on bone scaffold manufacturing process: A review", *Heliyon*, (2022).
- [5]. Melocchi, A., et al., "A graphical review on the escalation of fused deposition modeling (FDM) 3D printing in the pharmaceutical field", *Journal of Pharmaceutical Sciences*, **109**, 10, p. 2943-2957, (2020).
- [6]. Pu'ad, N.M., et al., "Review on the fabrication of fused deposition modelling (FDM) composite filament for biomedical applications", *Materials Today: Proceedings*, **29**, p. 228-232, (2020).
- [7]. Tuazon, Brian & Custodio, Nick Anthony & Basuel, Rex & Reyes, Lanz & Dizon, John Ryan. "3D Printing Technology and Materials for Automotive Application: A Mini-Review". *Key Engineering Materials*. 913. 3. (2022). 10.4028/p-26o076.

- [8]. Yang, J.; Li, B.; Liu, J.; Tu, Z.; Wu, X. "Application of Additive Manufacturing in the Automobile Industry: A Mini Review". *Processes*, 12, 1101, (2024).
- [9]. Karkun, Mohammad Suhel & Dharmalingam, Sathish. "3D Printing Technology in Aerospace Industry – A Review". *International Journal of Aviation, Aeronautics, and Aerospace* (2022). 10.15394/ijaaa.2022.1708.
- [10]. Martinez, Dan William & Espino, Michaela & Honelly Mae, Cascolan & Crisostomo, Jan Lloyd & Dizon, John Ryan. "A Comprehensive Review on the Application of 3D Printing in the Aerospace Industry". *Key Engineering Materials*. 913. 27-34. (2022). 10.4028/p-94a9zb.
- [11]. Adeleke, Adeniyi & Montero, Danny & Lottu, Oluwaseun & Ninduwezuor-Ehiobu, Nwakamma & Ani, Emmanuel. "3D printing in aerospace and defense: A review of technological breakthroughs and applications". *World Journal of Advanced Research and Reviews*. 21. 1149-1160, (2024).
- [12]. Marciniak, Marcin. "The 3D Printing in Military Applications: FDM Technology, Materials, and Implications". *Advances in Military Technology*. 18. 241-257, (2023).
- [13]. Đinh, Thế Dũng, Nguyễn, Trần Hùng, Lê Đức Dương, "Nghiên cứu tối ưu hóa quá trình kéo sợi và in 3D đối với vật liệu CF/PA6". *Tạp chí Khoa học và Công nghệ quân sự*, No 94, P. 55–61, (2024), (in Vietnamese).
- [14]. Miyabo, Atsushi. "Polyamide 11: New Material and Application Development of Castor Oil Based Engineering Plastics for Fiber Industries". *Sen'i Gakkaishi*. 67. P.351-P.356, (2011).

TÓM TẮT

Nghiên cứu chế tạo vật liệu in 3D composite trên nền blend của polyamide 6 và polyamide 11

Sợi in 3D CF/PA6+PA11 được tạo ra từ sự kết hợp giữa blend của nhựa polyamide 6 (PA6) của BASF, nhựa polyamide 11 (PA11) của Arkema và sợi cacbon của hãng Toray (Nhật Bản). Nghiên cứu này tập trung vào việc đánh giá tỷ lệ blend của pa6, pa11 và tỷ lệ phối trộn của blend với sợi cacbon trong chế tạo sợi in 3D. Các thông số kỹ thuật quan trọng như độ bền kéo, độ bền uốn cùng độ bền va đập đã được đo đạc để đánh giá hiệu suất cơ học trong các điều kiện chế tạo sợi in. Nghiên cứu đã xác định rằng, blend với tỷ lệ thành phần hàm lượng nhựa PA6:PA11 là 70:30 cho hiệu quả tương hợp tốt nhất. Trên cơ sở blend của PA6 và PA11, sợi in 3D CF/PA6-PA11 đạt độ bền cơ tính phù hợp khi hàm lượng thành phần của PA6, PA11 cùng sợi cacbon kích thước ngắn ($\leq 0,3$ mm), sợi cacbon kích thước dài (0,3 mm - 1 mm) lần lượt là 49%, 21%, 20% và 10%.

Từ khóa: In 3D; Vật liệu composite; Polyamide 6; Sợi cacbon.