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ANNEALING EFFECT ON IMPACT PROPERTIES OF REINFORCED POLYMER PA6-GF MADE BY FDM TECHNOLOGY

UTICAJ ŽARENJA NA UDARNA SVOJSTVA OJAČANOG POLIMERA PA6-GF IZRAĐENOG FDM TEHNOLOGIJOM

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- Charpy impact properties

Ključne reči
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- žarenje
- svojstva udarne žilavosti

Abstract

Use of composite materials has seen significant growth, especially in the manufacture of lightweight structures and biomedical applications. One type of composite material is made up of polymer materials reinforced with glass fibres. PA6-GF reinforced with 25 % chopped glass fibres is a representative of this composite material group. The manufacturer recommends annealing as a heat treatment process after production. However, annealing requires additional equipment and time. This paper seeks to investigate the effect of non-annealed PA6 GF on the Charpy impact properties. Samples for Charpy impact property tests are defined according to BAS EN ISO 179-2:2021. The test specimens were printed on the FlashForge Creator 3 PRO printer, and the testing was performed on the AMSLER RPK300 device.

Izvod

Upotreba kompozitnih materijala već je doživela masovnu ekspanziju pre svega u izradi lakih konstrukcija i u biomedicinskim primenama. Jednu grupu kompozitnih materijala čine i polimerni materijali ojačani staklenim vlaknima. Kao predstavnik ove grupe materijala izabran je PA6-GF ojačan sa 25 % staklenih vlakana. Prema prospektu proizvođača, nakon izrade delova preporučuje se žarenje. Žarenje kao proces termičke obrade iziskuje dodatnu opremu kao i dodatno vreme. Ovaj rad ima za cilj da utvrdi uticaj izostavljenog preporučenog žarenja na svojstva udarne žilavosti PA6 GF. Uzorci za ispitivanje svojstava žilavosti definisani su prema BAS EN ISO 179-2:2021, a epruvete su izrađene na Flash Forge Creator 3 PRO štampaču, dok je ispitivanje udara obavljeno na AMSLER RPK300 uređaju.

INTRODUCTION

Composite materials are widely used in the development of lightweight structures and many biomedical applications. A clear example of this claim can be found in the fact that such materials are increasingly used in the automotive industry. Requirements for weight reduction come primarily from the need to reduce fuel consumption and develop more energy-efficient vehicles. Also, reducing the weight of existing components enables the installation of additional safety systems as well as emission control systems, /1, 2/.

Composite materials, primarily due to their mechanical properties, are used in many dental and cardiovascular applications, as well as for joint prostheses, artificial ligaments, etc. In recent years, there has been active research on nylon composites in tissue engineering as a substitute for metallic implants, owing to nylon's biocompatibility and its capacity for favourable chemical stability and adjustable mechanical properties. These attributes make nylon and its derivatives highly sought after for such applications, with promising potential for promoting bone growth due to their appropriate bioactivity, /3, 4/.

One group of composite materials consists of polymer materials reinforced with glass fibres. For this research, PA6-GF reinforced with 25 % chopped glass fibres produced by PolyMide™ was chosen. The reason for this lies in its availability on the market, as well as the fact that the process of making parts from this material requires high and controlled printing temperatures (at least above 280 °C), the use of additional aids (such as glue), very abrasive, requiring frequent change of printing nozzles or the use abrasive resistant nozzles. It is also recommended to anneal all parts after manufacturing.

Annealing as a heat treatment process requires additional equipment and time. The main goal of this paper is to research the effect of omitting recommended annealing on the Charpy impact properties of the PA6 GF.

LITERATURE REVIEW

The study /5/ explores how different levels of irradiation affect the morphological and mechanical properties of three polyamide grades, including unreinforced and glass fibre-reinforced types. By subjecting them to irradiation doses ranging from 0 to 200 kGy, the researchers characterised the resulting changes using various analytical methods. The findings show significant alterations in morphology and improved mechanical properties due to irradiation.

The core focus in article /6/ is accelerated aging behaviour of a specific polyamide grade, reinforced with glass fibre and heat stabilised. The study utilised hot air exposure (HAE) and pressure cooker testing (PCT) at elevated temperatures to simulate accelerated aging. Key findings include the detection of characteristic aging indicators such as superficial thermal oxidation for HAE and the development of a regular crack pattern and surface roughening for PCT. These changes were accompanied by a significant reduction in molar mass and degradation in mechanical performance with material cracking observed when the molar mass reached approximately 25 % of its initial value.

Research /7/ investigates how different weight percentages of glass fibre reinforcement impact mechanical properties of nylon (PA6) composite. Test specimens with varying compositions, ranging from pure nylon to nylon with 20 % glass fibre, were prepared using injection moulding. Tensile and impact tests were conducted to evaluate the mechanical properties. The results demonstrate a significant influence of glass fibre content on the nylon composites. Specifically, the elasticity modulus and yield strength increase with higher glass fibre percentages, with the 80 % nylon + 20 % GF composite exhibiting the highest values. Conversely, pure nylon has the lowest tensile strength, while the 80 % nylon + 20 % GF composite shows the most substantial improvement. Elongation at break is highest for pure nylon but decreases with increasing glass fibre content. Impact strength varies across compositions, with the 85 % nylon + 15 % GF composite displaying the highest toughness and the 95 % nylon + 5 % GF composite exhibiting the lowest.

Primary focus in /8/ is to investigate and evaluate the impact resistance and behaviour of Nylon-6, a commonly used FDM engineering material, along with two of its composites: PACF and PAGF30. Through Charpy impact testing using both U- and V-notch specimens, the authors assessed the impact strength of these materials and analysed the fractured surfaces using SEM. The key finding indicates that the impact strength of the nylon composites surpasses that of pure nylon, with PAGF30 exhibiting the highest improvement, absorbing 18.6 % more impact energy than PACF and 210.56 % more than pure Nylon-6. Fractography analysis reveals that the failure mechanisms involved fibre pull-out, fibre breakage, matrix deformation, and interface delamination.

Study /9/ found that adding fibres significantly increases the tensile strength of Continuous Fibre Reinforced Additively Manufactured (CFRAM) parts, with up to a 2200 % improvement. Increasing fibre content enhances overall tensile performance. Carbon fibre (CF) reinforcement shows superior performance compared to fibreglass (FG) and Kevlar. CFRAM parts have the potential to replace metals and conventional composites in industries like automotive engineering.

Xiaojiang Liu et al. /10/ highlight a significant advancement in additive manufacturing: a high-temperature annealing process that enhances the mechanical strength of Multi Jet Fusion (MJF)-printed polyamide 12 (PA12) and GF/PA 12 composites. Despite MJF's efficiency, these materials typically exhibit lower mechanical strength compared to commercial polymer composites. However, through the novel application of a high-temperature annealing process (173 °C), the mechanical strength of both PA12 and GF/PA12 specimens is significantly improved. This enhancement, primarily attributed to increased crystallinity, suggests broader applications across SLS- and MJF-printed polymers and composites.

Study /11/ investigates the influence of temperature on impact energy for continuously fibre additively manufactured (AM) polymer matrix composites. Utilizing a nylon-based matrix and four continuous reinforcements (fibreglass, high-temperature fibreglass (HSHT), Kevlar, and carbon), the tested temperatures ranged from -40 to 90 °C. Employing a previously identified optimal lattice structure and fibre volume configuration, impact tests reveal the best performance order: fibreglass, HSHT, Kevlar, and carbon. However, impact resistance decreases below ambient temperatures and above 50 °C. Each material's impact energy is modelled using third-degree polynomials, with correlation factors exceeding 92 %. Additionally, failure analysis identifies matrix cracking, delamination in the printing direction, fibre tearing, and fibre pulling as primary failure mechanisms.

Research /12/ aims to enhance impact strength without compromising tensile strength in polyamide 6 (PA 6) and short glass fibre reinforced PA 6 (GFPA 6), common materials in sports equipment. Ternary nanocomposites for PA 6, featuring nanoclay as a strengthening agent and ethylene-octene elastomer grafted maleic anhydride (POE-g-MAH) as a toughening agent, significantly increases impact strength by over 140 % while maintaining tensile properties. For GFPA 6, formulation and process optimisation prevent glass fibre length reduction, and the addition of 5 % POE-g-MAH increases impact and tensile strength by 145.4 % and 8.9 %, respectively.

Study /13/ investigates the relationship between the molecular mobility of the amorphous phase in polyamide 6,6 (PA 66) and its mechanical properties. By examining PA66 formulations with varying glass transition temperatures (T_g) achieved through different methods, such as additivities and chemical modification, the study focuses on impact strength using instrumented Charpy impact tests across a broad temperature range. The key finding highlights a strong correlation between the brittle-tough transition temperature ($T_{B/T}$) and the T_g of the samples, underscoring the significance of T_g in determining the mechanical behaviour of PA66 formulations.

Michael Handwerker et al. /14/ investigate the influence of an annealing process on the mechanical performance of continuous and chopped fibre-reinforced polyamide 6 in the build-up direction. They concluded that Young's modulus increases by a factor of three, while ultimate tensile strength (UTS) increases by 50 % for the chopped carbon fibre-reinforced material, and by 186 % for the continuous glass fibre-reinforced material.

Qingyu Meng et al. /15/ investigate the annealing effect on the crystalline structure and mechanical properties of long glass fibre-reinforced polyamide 66 (LGF-PA66) composite. Through experimental studies, the research systematically examines the impact of annealing temperatures ranging from 120 to 200 °C on composite properties. The results indicate that while annealing negligibly affects the crystallinity and crystal morphology of LGF-PA66 composite, it significantly promotes phase transition and crystal growth. Moreover, annealing leads to a notable increase in tensile and flexural properties but reduces impact strength, accompanied by a shift in failure mode. These changes in mechanical properties are attributed to crystal transition, matrix strengthening, and release of residual stress induced by the annealing process.

Previous research primarily focuses on the analysis of various influencing factors on ultimate tensile strength and flexural strength of this and similar materials, primarily due to specific and expensive equipment required for testing impact strength. It can be concluded that annealing affects first of all the UTS and flexural strength of polymers reinforced with glass fibres of parts made using Multi Jet Fusion, Selective Laser Sintering, injection moulding, and Fused Deposition Modelling.

MATERIALS AND METHOD

PA6-GF reinforced with 25 % chopped glass fibres, produced by PolyMide™, is chosen for this research, as stated previously. The chosen material is very hygroscopic (susceptible to absorbing moisture from the atmosphere). Material is stored without any special additional equipment (such as the Dry Box system), in the original box, and it is important to note that it was used without any dehumidification process. The mechanical and thermal properties of this material are presented in Table 1.

Specimens were defined according to /17/. The designation of specimen type and direction of blow is IS0 179-1/3p /18/ (unnotched) with dimensions 10×4×55. Specimens were printed using FlashForge Creator 3 Pro printer. The main reason for using this printer is the closed printing chamber which eliminates the possibility of external influences on sudden temperature variations. FlashForge Creator 3 Pro also offers the ability to constantly monitor and modify the temperatures of both the extruder and the printing plate, which is significant due to the demanding nature of the material itself. Printing parameters are defined using the recommendation of the material supplier and are presented in Table 2. The specimen in the FlashPrint 5 software after defining the printing parameters is shown in Fig. 1.

Table 1. Mechanical and thermal properties of PA6-GF, /16/.

Mechanical properties (moisture conditioned)	Young's modulus	2053 ± 243 MPa
	Tensile strength	50.8 ± 4.9 MPa
	Charpy impact strength	21.2 ± 1.1 kJ/m^2
Thermal properties	Melting temperature	214.5 °C
	Glass transition temperature	70.4 °C
	Crystallization temperature	174.5 °C

Before each print, the platform was cleaned with alcohol, and a thin coat of Magigoo PA adhesive was applied to ensure adequate adhesion between the platform and specimen. Three specimens were produced for Charpy impact properties test. All specimens were conditioned at room temperature for 20 days after production, without the recommended annealing.

Table 2. Printing parameters.

Nozzle size	0.4 mm
Layer height	0.19 mm
Extruder temperature	290 °C
Platform temperature	45 °C
Base print speed	36 mm/s
Top solid layers	4
Bottom solid layers	4
Fill density	100 %
Fill pattern	Line
Start angle	45°
Cross angle	90°
Cooling fan	OFF

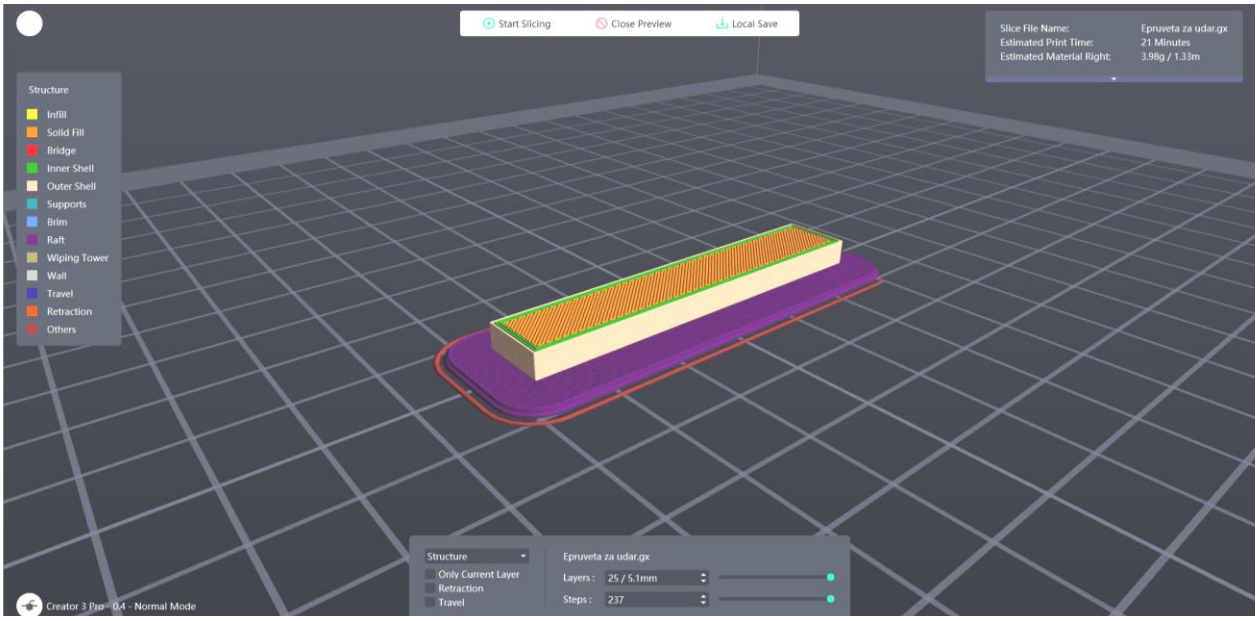

Figure 1. Specimen in FlashPrint 5® software.

Instrumented Charpy impact properties tests were performed at the University of Maribor, Faculty of Mechanical Engineering, using the AMSLER RPK300 Charpy pendulum (Fig. 2).

Figure 2. AMSLER RPK300, /19/.

RESULTS AND DISCUSSION

Results of these tests are shown on diagrams - change in force with time and energy with time, i.e., the force-time and absorbed energy-time curves. In Figs. 3-5 those curves represent all testing specimens.

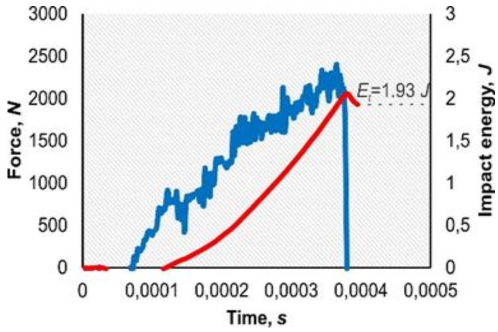

Figure 3. Force-time and energy-time curves for specimen 1.

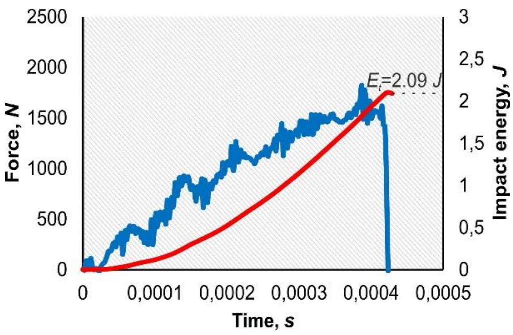

Figure 4. Force-time and energy-time curves for specimen 2.

The total energy (E_t) can be divided into energy absorbed for crack initiation (E_i) and energy for crack propagation (E_p). The total energy is spent on crack initiation for all three specimens, so we can conclude that PA6-GF is a brittle material - after crack initiation the material is not able to resist crack propagation.

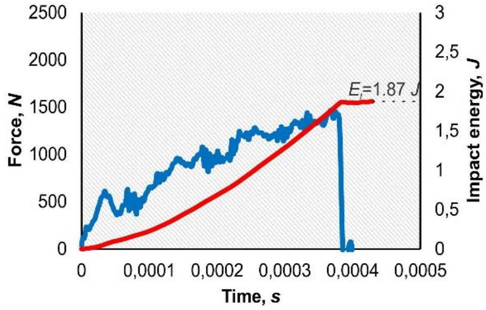

Figure 5. Force-time and energy-time curves for specimen 3.

In Table 3 both Charpy impact strength and impact energy are given. It can be concluded that Charpy impact properties increase by a factor of more than 2 for specimens tested without annealing. Furthermore, from the aspect of impact properties, it is advisable to omit this treatment.

Table 3. Charpy impact strength and impact energy.

	Impact energy	Charpy impact strength
Specimen 1	1.93 J	48.25 kJ/m^2
Specimen 2	2.09 J	52.25 kJ/m^2
Specimen 3	1.87 J	46.75 kJ/m^2

CONCLUSIONS

The main goal of this paper is to determine the influence of omitted recommended annealing on the Charpy impact properties of PA6-GF specimens obtained by FDM technology.

The research confirmed the thesis that PA6-GF is a brittle material because all impact energy is spent only on crack initiation.

It has also been proven that annealing can be eliminated, which will not affect the decrease in Charpy impact properties. On the contrary, the impact properties are significantly increased. This fact is of great importance because it provides savings in terms of additional time after production, but also savings in the purchase of additional annealing equipment, especially since PA6-GF has a demand for strictly controlled manufacturing conditions.

Further research should be aimed at defining unique parameters and processes that would affect the improvement of all (or most) of the mechanical properties of this material, because parts in reality are always exposed to loads that generate complex stress conditions.

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