

Anna Makuch<sup>1,2\*</sup>, Maria Trzaska<sup>1</sup>, Konstanty Skalski<sup>1</sup>, Marcin Bajkowski<sup>2</sup>

<sup>1</sup> Institute of Precision Mechanics, ul. Duchnicka 3, 01-796 Warsaw, Poland

<sup>2</sup> Warsaw University of Technology, Department of Construction Engineering and Biomedical Engineering, ul. Narbutta 85, 02-524 Warsaw, Poland

\*Corresponding author: E-mail: a.makuch@wip.pw.edu.pl; anna.makuch@imp.edu.pl

Received (Otrzymano) 13.03.2015

## PA-G COMPOSITE POWDER FOR INNOVATIVE ADDITIVE TECHNIQUES

The paper presents the results of research concerning the influence of the method and parameters of mixing polyamide powder (PA2200) and graphene flakes (G) on the formation of a composite powder intended to produce a new composite material - PA-G by Selective Laser Sintering. The mixing process was carried out in a rotary mixer for different mixing durations: 1, 2, 4 and 8 hours. The research results of the influence of mixing time on the structure and homogeneity of the PA-G composite powder are presented. The completed studies have shown that mixing time has an impact on the uniform distribution of the disperse phase (graphene flakes) in the volume of the PA-G composite powder particles. The 8-hour mixing time caused mechanical bonding of the powder particles, in the form of so-called neck, which is typical for selective laser sintering of powders (SLS).

**Keywords:** polyamide, graphene, composite powder, selective laser sintering, rapid prototyping

## PROSZEK KOMPOZYTOWY PA-G DLA INNOWACYJNYCH TECHNIK PRZYROSTOWYCH

W pracy przedstawiono wyniki badań wpływu metody i parametrów mieszania proszku poliamidu PA2200 i płatków grafenu (G) na formowanie się proszku kompozytowego przeznaczonego do wytworzenia metodą selektywnego spiekania laserowego nowego materiału kompozytowego PA-G. Mieszanie proszków realizowano w mieszalniku rotacyjnym o różnych czasach trwania mieszania: 1, 2, 4 i 8 godzin. Przedstawiono wyniki badań wpływu czasu mieszania na strukturę i jednorodność proszku kompozytowego PA-G. Zrealizowane badania wykazały, że czas mieszania ma wpływ na równomierne rozmieszczenie fazy dyspersyjnej w postaci płatków grafenu w objętości cząstek proszku kompozytowego PA-G. Czas mieszania wynoszący 8 h powoduje efekt mechanicznego spajania cząstek proszku kompozytowego PA-G w postaci tzw. szyjki, który jest typowy dla procesu selektywnego spajania proszków (SLS).

**Słowa kluczowe:** poliamid, grafen, proszek kompozytowy, selektywne spajanie laserem, szybkie prototypowanie

## INTRODUCTION

The basis of rapid technological progress is inter alia, the intensive research on the development of new materials having favourable physicochemical properties. Composites have a huge potential concerning the possibility of developing new material properties. Composite materials made of different phases are characterised by properties which are unattainable for conventional "monolithic construction materials." In this type of materials, more than in any other, their properties can be shaped and designed, which is done by appropriate selection of the components, shape and size of the particles of the disperse phase and their preparation process.

Incremental Techniques (Rapid Prototyping - RP, Rapid Manufacturing - RM), whose dynamic development was initiated in the 1980s, provide some new opportunities in the area of creating new materials, without the limitations of traditional technologies.

The leading method in the production of a powder material is SLS technology - Selective Laser Sintering.

In this technology, the primary input material is low-melting polyamide type 12, which can create not only prototypes, models, conceptual or functional products, but also short production runs of finished parts of less responsible assemblies, which are not exposed to significant dynamic loads (e.g. casings, screens, forms, connectors in the automotive, aerospace, electrical engineering industry, or templates in implantology and orthopaedics). The mechanical and thermal properties of components made of pure polyamide powder (PA2200) limits the application area of products made by means of this technique [1, 2]. In many centres, research is conducted to obtain more favourable properties of elastomers or polymers by the addition of a reinforcement in the form of carbon fibres, carbides, nitrides, or ceramics [3]. The results of these studies demonstrate that such enhanced polymer materials have increased mechanical, physical or thermal properties, on condition that preparation of the ingredients was proper and appropriate technological parameters were applied.

The results of work on the enrichment of polymers by carbon allotrophic varieties: fullerenes [4], graphene [5-9], or nanotubes [10, 11] are promising. These studies are mainly focused on such materials as: aniline, polyethylene, ethyl methacrylate and nylon and on processing them with the use of traditional technologies. Conducted preliminary studies show that the field of application of polyamide used in RP technology can be extended by introducing a dispersion phase in the form of graphene flake G in order to obtain a new composite material: graphene - polyamide (PA-G) which has improved mechanical properties.

Achieving a homogeneous composite powder is crucial in order to obtain favourable physical-chemical properties of the new composite due to the nature of the SLS process.

The aim of the conducted study was to determine the influence of the method of composite powder preparation and mixing time on its parameters such as: uniformity, structure, bulk density, etc. The percentage share of the ingredients and the method of their preparation for the SLS process determine the porosity and proper structure of the gained composite material.

## RESEARCH METHODS

Polyamide powder type 12, with a spherical particle shape (according to PN-EN ISO 3252: 2002) and graphene flake powder produced by Graphene Chemical Industries Co. were used for the production of the PA-G composite powder. According to the manufacturer's data, the thickness of the graphene flakes was  $5\div 8$  nm, and their area  $120\div 150$   $\text{m}^2/\text{g}$ . The polyamide-graphene (PA-G) composite powder was made as a result of mixing the polyamide (PA) 99% by weight and graphene flakes (G) 1% by weight in a rotary powder mixer. The powder mixing time was 1, 2, 4 and 8 hours. During the mixing process, the mixer container was tilted at an angle of  $30^\circ$  and it spun at a velocity of 56 rev/min. Four types of PA-G composite powder were prepared, differing in homogenisation times in the mixer. The studies of the polyamide (PA), graphene (G) and composite (PA-G) powders were carried out by means of a 2D optical microscope (ECLIPSE LV150 NICON coupled with a computer image analyzer NIS-Elements BR 3.0), a 3D microscope (Keyence VHX 5000), a scanning electron microscope - SEM (ZEISS) and a Raman spectrometer.

## RESEARCH RESULTS

Graphene in the form of polydisperse flakes was used to prepare the PA-G composite powders. An SEM image and the Raman spectrum of the graphene flakes are shown in Figure 1.

The graphene flakes used to manufacture the PA-G composite powders are characterized by a great diversity of dimensions. The broadened peak at (2D)

$2700\text{ cm}^{-1}$  of the recorded Raman spectrum, characteristic for the individual layers of graphene, shows that the applied powder contains multilayer graphene flakes.

An image of the polyamide (PA) powder used to prepare the composite powder, and its Raman spectrum are shown in Figure 2.

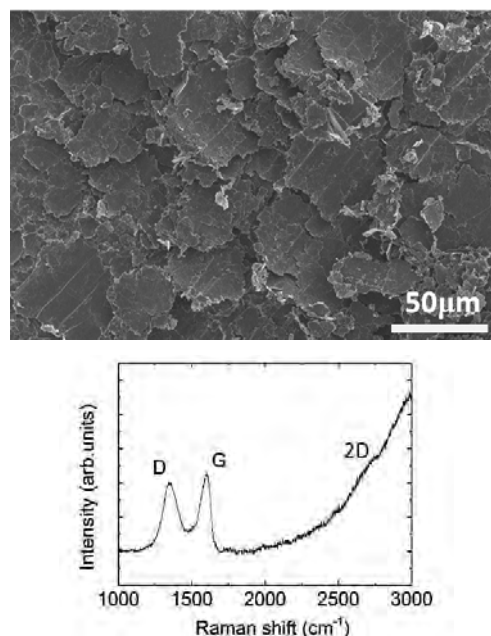


Fig. 1. SEM image and Raman spectrum of graphene flakes  
Rys. 1. Obraz SEM i widmo Ramana płatków grafenu

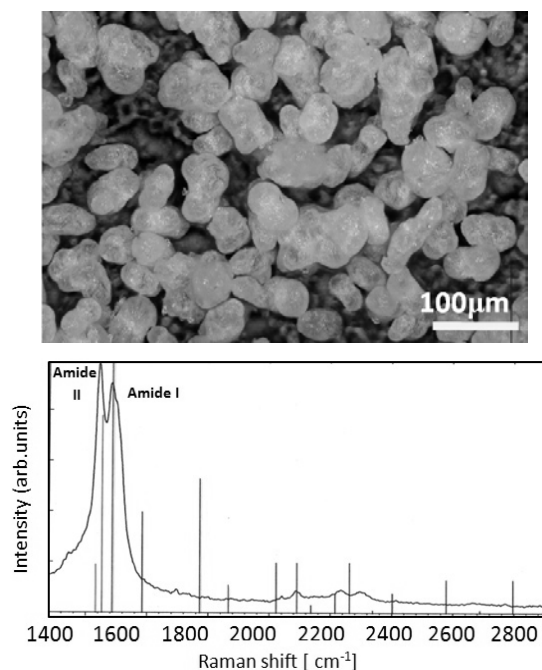


Fig. 2. Image of particles and Raman spectrum of PA powder  
Rys. 2. Obraz cząstek oraz widmo Ramana proszku PA

The PA powder particles are characterized by a spherical shape and a slight variation of their dimensions ( $\sim 60$   $\mu\text{m}$ ). There is a double absorption band in the Raman spectrum of the PA2200 polyamide powder. The first peak ( $1510\text{ cm}^{-1}$ ) indicates the pres-

ence of alkyl and aryl groups at the N amide II ( $C_2H_5NO_4 \cdot 0.5H_2O$  - Ammonium Hydrogen oxalate Hydrate). The second peak ( $1630\text{ cm}^{-1}$ ) belongs to the carbonyl group ( $C=O$ ) and the acyl group of the I amide ( $NH_2 \cdot CO \cdot NH_2$ ).

In the process of preparing a composite mix, it is important to choose the right size of particles of the components and the method of their preparation and mixing. In the case of the graphene-polyamide composite (PA-G), we are dealing with components of different properties and density (specific gravity of the polyamide powder is  $0.44\text{ g/cm}^3$  and graphene is  $2\text{ g/cm}^3$ ).

and 8 hours of mixing (Fig. 3c, 3d, Fig. 4), it is possible to notice the formation of agglomerates of the powder matrix with the embedded graphene flakes in the volume of the PA grains.

Using a computer image analysis method, measurement of the graphene percentage in the produced PA-G composite powder after different mixing times was made (Table 1). Analysis of the results shows that the surface share of graphene is 3 times higher in the mix composite than the original mass fraction (1%) and it slightly increases together with an increase in the mixing time (Fig. 5).

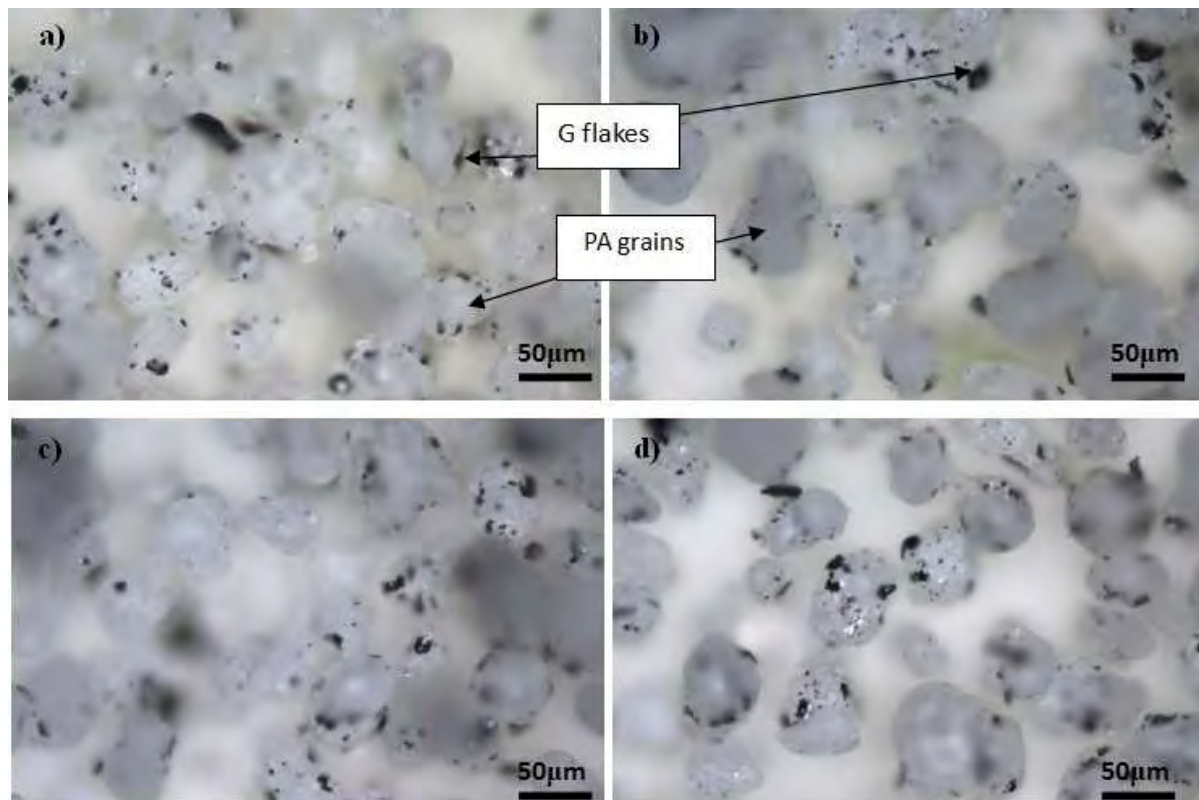


Fig. 3. Images of PA-G composite powder particles after various mixing times: 1 h (a), 2 h (b), 4 h (c), 8 h (d)

Rys. 3. Obrazy proszku kompozytowego po różnych czasach mieszania: 1 h (a), 2 h (b), 4 h (c), 8 h (d)

The composite components also differ in shape and particle size ( $\sim 60\text{ }\mu\text{m}$  polyamide, graphene - different dimensions of a few microns). Graphene is in the form of two-dimensional flakes, polyamide is characterized by a spherical shape.

Images of the PA-G composite powder particles after various mixing times are shown in Figure 3.

The PA-G composite powder after 1 hour mixing time is characterized by collocation of the graphene flakes mainly in the surface layers of the soft polyamide PA2200 particles (Fig. 3a). After 2 hours of mixing it was possible to observe plastic deformation of the spherical polyamide grains resulting from interaction of the component particles and the steel directional ribs of the rotary mixer. As a result, rounding and flattening of the grains followed these interactions (Fig. 3b). After 4



Fig. 4. Image of PA-G composite powder particles after 8 - hour mixing time

Rys. 4. Obraz cząstek proszku kompozytowego PA-G po 8 h mieszania

TABLE 1. Percentage surface share of graphene in PA-G composite powder

TABELA 1. Powierzchniowy udział procentowy grafenu w proszku kompozytowym PA-G

1 h	grafen [%]	2 h	grafen [%]
sample 1	2.91	sample 1	2.9
sample 2	3	sample 2	3.6
sample 3	3.2	sample 3	2.8
sample 4	3.3	sample 4	3
sample 5	3.1	sample 5	3.5
sample 6	3.2	sample 6	3.9
sample 7	3.1	sample 7	3.3
Mean	3.12	Mean	3.29
Std Deviation	0.1319	Std Deviation	0.4049
4 h	grafen [%]	8 h	grafen [%]
sample 1	3.32	sample 1	3.28
sample 2	3.41	sample 2	3.54
sample 3	3.32	sample 3	3.31
sample 4	3.43	sample 4	3.3
sample 5	3.5	sample 5	3.45
sample 6	3.27	sample 6	3.34
sample 7	3.23	sample 7	3.38
Mean	3.35	Mean	3.37
Std Deviation	0.0957	Std Deviation	0.0939

Images of the surface morphology of the PA powder grains and particles of the PA-G composite after different mixing times are shown in Figure 6.

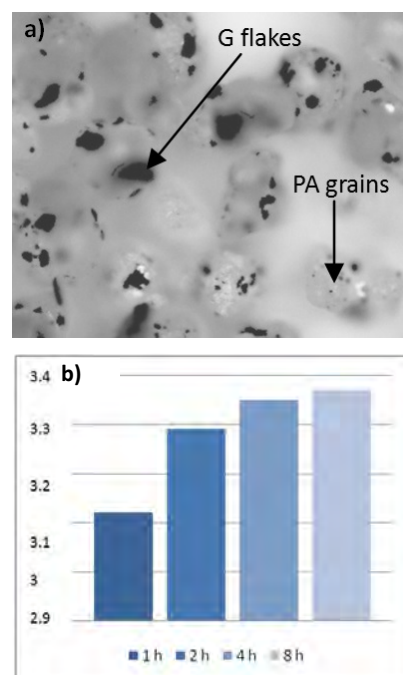


Fig. 5. Surface share of graphene in PA-G composite powder: measurement method (a) and diagram of impact of mixing time on percentage share (b)

Rys. 5. Powierzchniowy udział grafenu w PA-G: sposób pomiaru (a) i wykres wpływu czasu mieszania na udział procentowy (b)

The images of the surface morphology of the powder particles (Fig. 6) show how polyamide matrix plasticization and the change in their shape increase proportionally to extension of the mixing time. Graphene (G) flakes (Fig. 6c, d) can be seen on the surface of the powder particles of the PA-G composite.

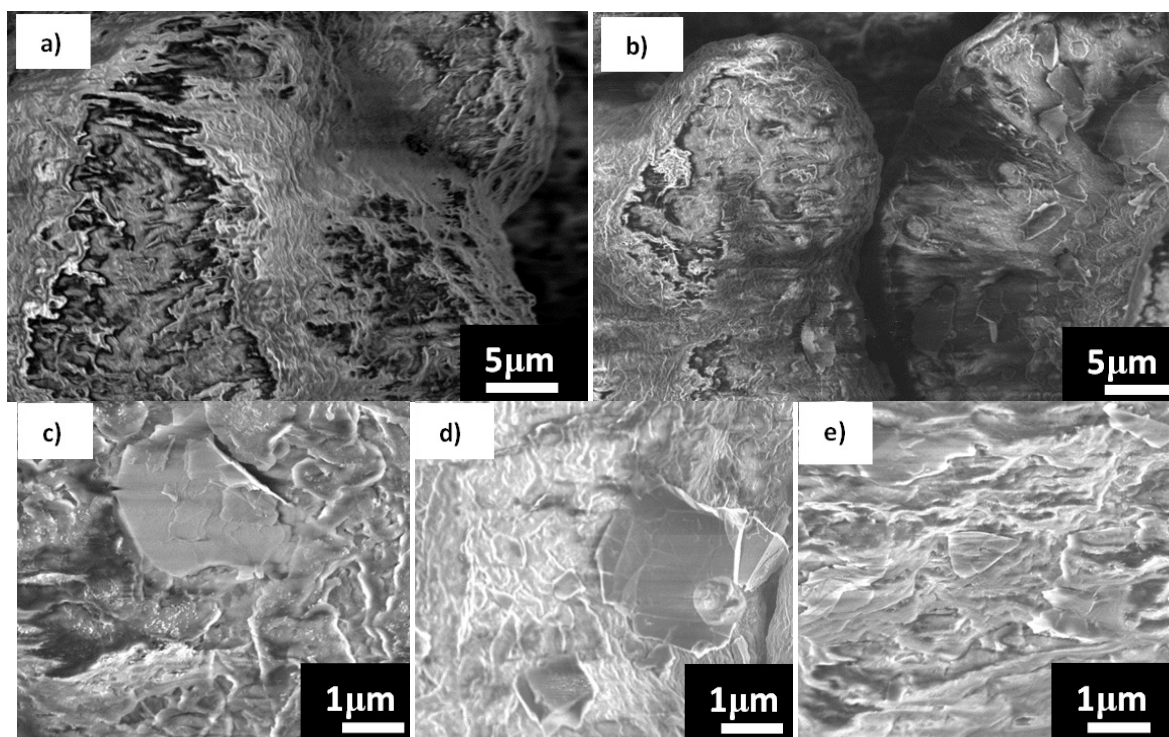


Fig. 6. Images of (SEM) morphology of PA powder grains (a) and PA-G powder particles after different mixing times: b) 1 h, c) 2 h, d) 4 h, e) 8 h  
Rys. 6. Obrazy (SEM) morfologii cząstek proszków PA (a) oraz kompozytowych PA-G po różnych czasach mieszania: b) 1 h, c) 2 h, d) 4 h, e) 8 h

Figure 7 shows the influence of extension of the mixing time up to 8 hours on initiating the process of mechanical bonding of the PA-G composite powder particles in the form of the "neck" phenomenon - typical for the selective laser sintering process of polymer powders (SLS) [11].

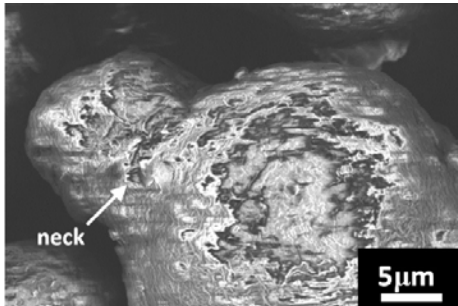


Fig. 7. Image of mechanical bonding phenomenon of PA-G composite powder particles after 8-hour mixing time - "neck" phenomenon

Rys. 7. Obraz efektu mechanicznego spajania cząstek proszku kompozytowego PA-G po 8 h mieszania - tzw. efekt szyjki

The formation of the neck is described by relationship (1), which determines the occurrence of the bonding phenomenon in that incremental bonding technology [11]:

$$a_{\max} = R \cdot \sin(\varphi/2) \quad (1)$$

where:

$a$  - the diameter of the neck formed at the border of the powder particles in the sintering process,  
 $R$  - average radius of the powder grain,  
 $\varphi$  - the angle between tangents to the surface of the sphere at the connecting section.

## PRELIMINARY SINTERING TRIALS

For a preliminary trial of producing a final new PA-G composite, the mix with the highest homogeneity (i.e., 8 h mixing time) was selected. The prepared and tested composite powder was evenly distributed on the ceramic substrate as a thin layer (0.5 mm) sample and sintered at the temperature of 175°C.

Images of the distribution of graphene in the PA-G composite material produced by the sintering process are shown in Figure 8.

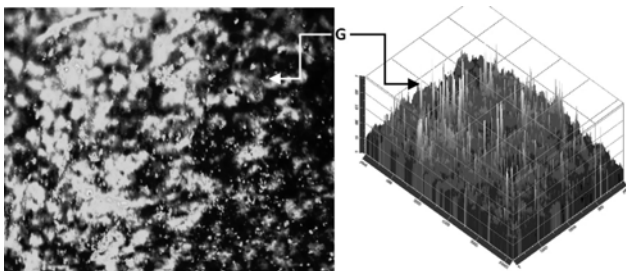


Fig. 8. 2D and 3D images of graphene collocation in PA-G composite material

Rys. 8. Obrazy 2D i 3D rozmieszczenia G w materiale kompozytowym PA-G

## CONCLUSIONS

The conducted studies as a result of the successive stages of homogenization of the mixture of the PA and G powders allowed assessment of the influence of mixing time on homogenization of the PA-G composite powder structure. The accomplished studies have shown that mixing in a rotary mixer causes both fragmentation of the graphene flakes and a change in the shape of the polyamide matrix grains, it also causes, depending on the mixing time, at first the arrangement of the graphene nanoflakes on the surface of the polyamide (1 h), and then their embedding in the whole volume of the 10-fold larger grains of the matrix (4 h, 8 h mixing times).

Prolongation of the mixing time also causes increased plasticization of the polyamide grains because of the mechanical interaction of the particles. On the other hand, increasing this time up to 8 hours leads to initiation of the process of mechanical bonding of the composite powder particles and to appearance of the "neck" phenomenon - typical for selective laser sintering of powders (SLS).

The conducted studies showed that the method used to prepare the composite powder in a rotary mixer and the adopted parameters of the mixing process provide a homogeneous structure of the PA-G composite powder.

Thus, the test results provide a good basis for manufacturing a new PA-G composite from graphene and polyamide powders by selective laser sintering (Rapid Prototyping technology).

## Acknowledgements

*This work was supported by the National Centre for Research and Development - Project No PBS1/A6/10/2012*

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