Hybrid polymer materials with substantially improved mechanical properties
(Sponsored article)

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Abstract: The results of the research project POIR.01.01.01-00-0760/18 implemented from the funds of the Smart Growth Operational Program in the years 2014-2020 entitled "Development of a new technology for manufacturing details from polymer materials with significantly improved mechanical and visual properties" at Splast Ltd. were presented. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to assess the structure of the composites. The strongest interactions at the composite–coating interface were observed in the case of the use of varnish (interphase boundary width). The composites were characterized by gloss in the range of 32.6–448 GU, which classifies them as semi-gloss or glossy materials. SEM micrographs confirmed the correctness of the selection of materials, as evidenced by good fiber dispersion in the polymer matrix, while maintaining a characteristic round shape.

Keywords: polymer composites, injection molding, carbon fiber, glass fiber, coatings.

Hybrydowe materiały polimerowe o ulepszonych właściwościach mechanicznych
(Artykuł sponsorowany)

Streszczenie: Przedstawiono wyniki badań projektu POIR.01.01.01-00-0760/18 realizowanego ze środków Programu Operacyjnego Inteligentny Rozwój w latach 2014–2020 pt. „Opracowanie nowej technologii wytwarzania detali z materiałów polimerowych o znacząco poprawionych właściwościach mechanicznych i wizualnych" w Splast Sp. z o.o. Do oceny struktury kompozytów użyto mikroskopię sił atomowych (AFM) i skaningową mikroskopię elektronową (SEM). Najsilniejsze oddziaływania na granicy faz kompozyt–powłoka zaobserwowano w przypadku zastosowania powłoki lakierniczej (szerokość granicy międzyfazowej). Kompozyty charakteryzowały się połyskiem w zakresie 32,6–448 GU, co klasyfikuje je jako materiały z półpołyskiem lub połyskiem. Mikrofotografie SEM potwierdziły poprawność doboru materiałów, o czym świadczy dobra dyspersja włókna w osnowie polimerowej, przy zachowaniu charakterystycznego okrągłego kształtu.

Słowa kluczowe: kompozyty polimerowe, wtryskiwanie, włókno węglowe, włókno szklane, powłoki.

Due to the rapidly developing technologies of polymer processing and the growing needs of the market, the properties of ordinary materials do not meet expectations. For this reason, there is an increasing need to search for new materials and methods of their processing. The development and production of composite materials has contributed to the significant development of the industry, because the properties of these materials have proven to be much better than those of traditional materials. Many different materials are used as reinforce-

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ment in composites, from natural to synthetic, depending on the purpose and application, size, form or required properties of the designed composite [1–3].

The mechanical strength of composite materials largely depends on the reinforcement used in them. A key aspect in composite design is that the designer has knowledge about the reinforcement, its types and properties, as well as awareness of the final purpose of the manufactured element. High-performance fibers are used as reinforcement in polymer composite parts. This group includes p-aramid, ultra-high molecular weight polyethylene (UHMWPE), glass, and basalt fibers. The most popular high-performance fiber is *p*-aramid, which has been closely associated with the arms industry for several decades. Fibers made of *p*-aramid have high longitudinal tensile strength and abrasion resistance. They are characterized by low density, high modulus, and the ability to absorb impact energy in the form of plastic deformation. They are also characterized by excellent thermal stability, maintaining their properties in a wide temperature range –196–427°C. The disadvantages of aramid fibers include sensitivity to UV radiation and poor resistance to compression. UHMWPE fibers, similarly, to aramid fibers, have excellent mechanical properties that are crucial for the composite industry. They exhibit high tensile strength and modulus. They have high resistance to impact, wear, friction, and chemicals. Additionally, they exhibit low moisture absorption. Unfortunately, UHMWPE fibers have a low melting point, which makes their application difficult. The high degree of crystalline and the lack of polar functional groups mean that these fibers have low surface energy. This translates into poor interfacial adhesion between the fiber and the matrix [5]. This forces UHMWPE fibers to modify their surface before they are used as reinforcement in composites. In the composite industry, glass fibers are used due to the favorable ratio of good properties to low prices. They are characterized by good mechanical properties that are stable at both low and high temperatures. In addition, glass fibers are characterized by good impact and fire resistance and low moisture absorption. However, they are sensitive to alkalis, phosphoric acid, have low modulus and low fatigue resistance. Currently, basalt fibers are experiencing a renaissance. During World War II, work on basalt fibers for military applications was conducted by both the USA and the Union of Soviet Socialist Republics. In the 1970s, interest in basalt in the USA decreased in favor of glass and aramid fibers. In recent years, many works have been written describing the possibility of using basalt in lightweight reinforcement composites or explosion-proof hatches. Scientists' interest in this material results from its unique properties. Basalt fibers are non-toxic and chemically stable. They have good mechanical properties, tensile strength, which is in the range of 3000–4000 MPa, and Young's modulus 80–110 GPa. The maximum operating temperature of basalt fibers is 1255°C Unfortunately, these fibers are brittle. They break easily during compression or impact tests. Basalt fibers have better properties than glass fibers and are cheaper than carbon fibers, which makes them a potential substitute [6].

Summarizing the above literature reports, it can be stated that each reinforcement, in addition to several advantages, also has certain disadvantages that eliminate it from the role of "ideal reinforcement". The solution to this problem is seen in multilayer hybridization of reinforcement, i.e., using several different types of reinforcing fibers at the same time. This hybridization allows for compensating the defects and synergies the positive features of the initial reinforcements, thus obtaining "ideal reinforcement". There are many ways to include several types of reinforcement in a composite. The most important of them are shown in Figure 1. Hybridization may consist in using several or all types of fiber reinforcement, e.g., fabric, mat, roving, 3D fabric, additionally made of different types of fiber [7–10].

This type of hybridization is called interlayer, which also includes combining fibrous and core reinforcements,

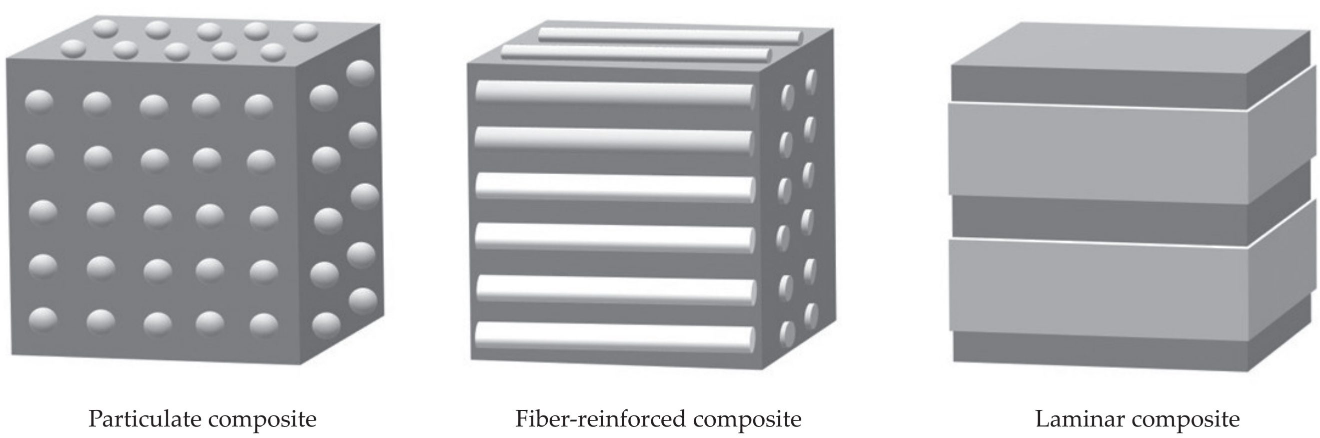

Fig. 1. Structure and type of polymer-based composites

e.g., synthetic or metal honeycomb structures, porous ceramic or polyurethane structures. In the case where two materials appear within one reinforcement layer (a fabric in which the weft and warp yarns are two different fibers), we are dealing with interlayer hybridization. Considering further, the yarn may consist of several types of fibers or fibers of the same type covered with a nanofiller or both possibilities at the same time [11–13].

Therefore, for over 35 years, Splast has been developing newer and newer technologies for obtaining and using composites based on thermoplastic polymers in the industry:
– automotive,
– electrical engineering,
– furniture,
– household appliances.

These activities involve the use of innovative production technologies to obtain such modern polymer materials, including:
– single- and multi-component injections,
– composite injection,
– MuCell technology,
– in-mold decoration (IMD),
– in-mold painting (IMP).

As part of the project "Development of a new technology for the production of polymeric material parts with substantially improved mechanical and visual properties", a production technology was developed based on the injection process of polymeric material parts reinforced with a carbon or glass mat (creation of a multilayer composite) and their varnishing or foil decoration. All production stages (creation of a reinforced composite, varnishing and foil application) were carried out in the injection process.

The result of the project was the development of a production technology based on the process of injection of elements made of polymer material reinforced with carbon or glass mat (creation of a multilayer composite) (Fig. 2) and their finishing with varnish or film.

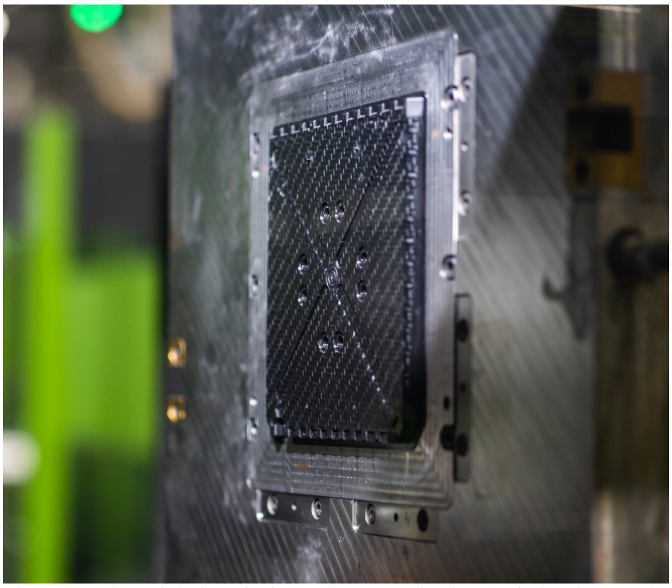

Fig. 2. Carbon fabric reinforced composite in the injection mold

All production stages (reinforced composite production, varnishing and film application) were carried out in the injection process.

Benefits from the process perspective include:
– injection of the reinforced part (over molding of the mat with polymer material) and the painting or film application process will be combined in one process;
– for painted parts, the production time will be shortened from 20 to 3 min, which is an 85% reduction in time;
– reduction in the number of rejects: painted parts will be reduced from 20 to 10%, parts with film will be reduced from 1 to 0.5%, which in both cases is a 50% reduction in the number of rejects.

From a product perspective:
– increased strength: flexural from 5 to 10 MPa (100% increase), tensile from 14 to 20 MPa (approx. 43% increase), Charpy impact strength from 50 to 60 kJ/m^2 (20% increase);
– increased scratch resistance under load: painted parts from 10 to 20 g (100% increase), film parts from 300 to 400 g (approx. 33% increase).

The research was conducted in cooperation with the Rzeszów University of Technology and the Chemnitz University of Technology.

The entire project implementation was divided into four stages:
– development of composite structures for use with decoration processes with full verification of mechanical properties (task implemented with TU Chemnitz) and with conducting detailed research in the field of structural and ageing tests (task implemented with Rzeszów University of Technology),
– production of prototype molds to evaluate materials developed in stage 1 using decoration technology,
– construction of a prototype line for evaluating the developed technologies,
– launching a prototype line with full automation and starting the production of parts.

At the stage of developing composite structures and testing the properties of the obtained composites using decoration technology, many studies were carried out covering the structure of the obtained composites and their aging properties, of which selected results of the studies using SEM and AFM of the obtained composites will be discussed in this publication.

EXPERIMENTAL PART

Raw materials and technology for obtaining composite plates

For the purposes of the research, composite plates were prepared in various configurations. The plates were made by assembling layers of unidirectional composite fabrics. The tested configurations are listed in Table 1 and Table 2.

The production of composite panels was carried out in the following steps:

T a b l e 1. General matrix-reinforcement configuration of the prepared plates

Reinforcement	Matrix		
	PA6	PA66	PP
GF (glass fiber)	X	X	X
CF (carbon fiber)	X	X	
GF + CF (glass and carbon fiber)	X		

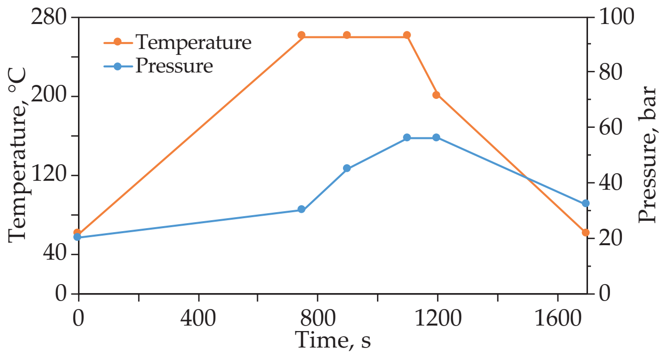

Fig. 3. Composite plate pressing parameters

T a b l e 2. Detailed configuration of the prepared plates

Reinforcement	GF	GF	GF	CF	CF	CF+GF
Matrix	PP	PA6	PA66	PA6	PA66	PA6
Volume fraction of fibers, %	47	47	41	41	41	41
Number of layers	10	10	7	14	14	10
Layer configuration	[0°/0°/90°/0°/0°]s	[0°/0°/90°/0°/0°]s	[90°/0°/0°/0°/0°/0°/90°]s	[90°/90°/0°/0°/0°/0°/0°]s	[90°/90°/0°/0°/0°/0°/0°]s	[90°/90°/0°/0°/0°]s
Thickness of one layer	0.19	0.22	0.3	0.14	0.14	0.14 CF/0.22 GF

s – denotes a symmetrical configuration of the composite plate layers, where the middle of the plate height is the plane of symmetry, so for the configuration [0°/0°/90°/0°/0°]s the fully described arrangement of layers is as follows [0°/0°/90°/0°/0°/0°/0°/90°/0°/0°].

T a b l e 3. Parameters of the plate pressing process

Reinforcement		GF	GF	GF	CF	CF	CF+GF
Matrix		PP	PA6	PA66	PA6	PA66	PA6
Heating	Temperature change in 30 min, °C	90-200	Fig. 3	60-270	Fig. 3	60-280	60-280
	Press pressure, bar	20		55		55	55
Cooling	Temperature change in 20 min, °C	200-90	Fig. 3	270-60	Fig. 3	280-60	280-60°C
	Press pressure, bar	15		30		30	30

– production of semi-finished products with fiber reinforcement in the form of tape;
– cutting the tape to dimensions of 260×260 mm;
– conditioning of semi-finished products for 24 h at a temperature of 60°C to remove residual moisture;
– compilation of the appropriate number of cut pieces of tape with fiber reinforcement and placing them, maintaining the appropriate order and angles of fiber arrangement, in the pressing mold;
– pressing the plate considering the temperature and pressure course appropriate for the fiber/matrix combination over time. An example pressing course is shown in Fig. 3, and the parameters in Table 3;
– removing the finished plate from the mold;
– bending the plate edges and further cutting the plates.

Then, the prepared plates were divided into two groups. The first group was evaluated, and the second group was cut into appropriate shapes and, after heating, placed in a prototype injection mold. Prototype parts were then injected in the shape shown in Fig. 4.

The tested prototype parts were prepared in the configuration presented in Table 4.

Methods

Analysis of the internal structure of composite parts covered with film or varnish

The analysis of the internal structure of composite parts covered with varnish or film was conducted using a Hitachi S-3400N scanning electron microscope (SEM) (Tokyo, Japan). The test samples were prepared using standard methods in accordance with ASTM E3 standard, using Struers (Copenhagen, Denmark) equipment.

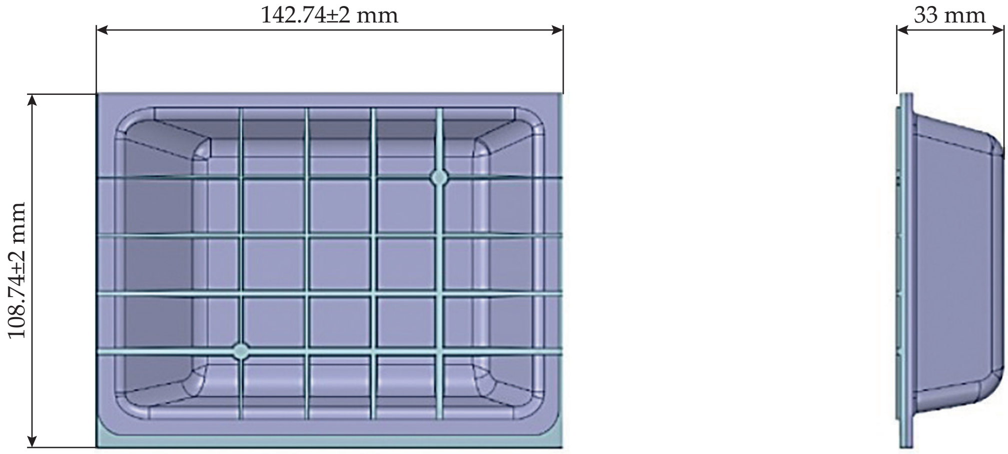

Fig. 4. View of the injection molded part shape

T a b l e 4. Types of prepared composite details

No.	Symbol
1	PP+PPGF+PUR
2	PA6+PA6CF+PUR
3	PA6+PA6GF+PUR
4	PA66+PA66CF+PUR
5	PA66+PA6GF+PUR
6	PA6+PA6CF+film
7	PA66+PA66GF+film
8	PA6+PA6GF+film II

where: the first member is the injected material, the second member is the type of composite plate used, and an additional decorative layer applied to the surface of the detail.

The studies included microscopic observations of cross-sections of the composites.

Imaging the composite coating interface was performed using an atomic force microscope (AFM). The measurement was performed in QNM mode using a Bruker Nanoscope V (Billerica, MA, USA) with a needle with a constant k = 40 N/m. Images were recorded at a scanning speed of 0.5 kHz and a resolution of 512 lines. By analyzing the local changes in Young's modulus on the surface of the composite film (varnish), the size of the contact area was determined.

Analysis of the structure of coatings in the form of varnish or film applied to the surface of composite elements

Analysis of the surface structure of the film or varnish applied to the surface of composite parts was performed using a Hitachi S-3400N scanning electron microscope (SEM).

Imaging of the coating surface was performed using an AFM atomic force microscope in Tapping Mode using a needle with a constant k=6 N/m. The measurement resulted in topography images and phase images, based on which, among other things, the surface roughness was determined.

The gloss of the coatings was measured at an angle of 20°, 60° and 85° using a Byk Gardner micro-TRI-gloss glossmeter in accordance with PN-EN ISO 2813.

RESULTS AND DISCUSSION

Structure analysis

Based on the SEM images presented in Fig. 5, no visible defects in the form of air bubbles or voids were observed in the polymer matrix. Moreover, the number of fibers, their shape and spatial arrangement can be observed. The images obtained confirmed the correctness of the selection of materials for the conducted processes, because the fibers are properly distributed throughout the area, maintaining a characteristic round shape. The spaces between the fibers are filled with polymer materials (PP, PA6, PA66). The lack of visible voids between CF and GF reflects the fact that the fibers are difficult to pull out of the polymer matrix due to the good interfacial adhesion with PP, PA6, PA66, respectively.

Based on the obtained DMT modulus images (based on the Derjaguin-Muller-Toporov model) of the cross-sectional area at the composite-coating interface, the width of the interphase boundary was determined (Fig. 6). The interphase region exhibits a transition modulus that is higher than the matrix modulus and lower than the fiber

T a b l e 5. Composite/coating interface width

Symbol	Interface width, nm
PA66+PA66GF+PUR	110
PA66+PA66CF+PUR	106
PA6+PA6GF+PUR	78
PA6+PA6CF+PUR	85
PP+PPGF+PUR	44
PA66+PA66GF+film	15
PA6+PA6CF+film	12
PA6+PA6GF+film II	18

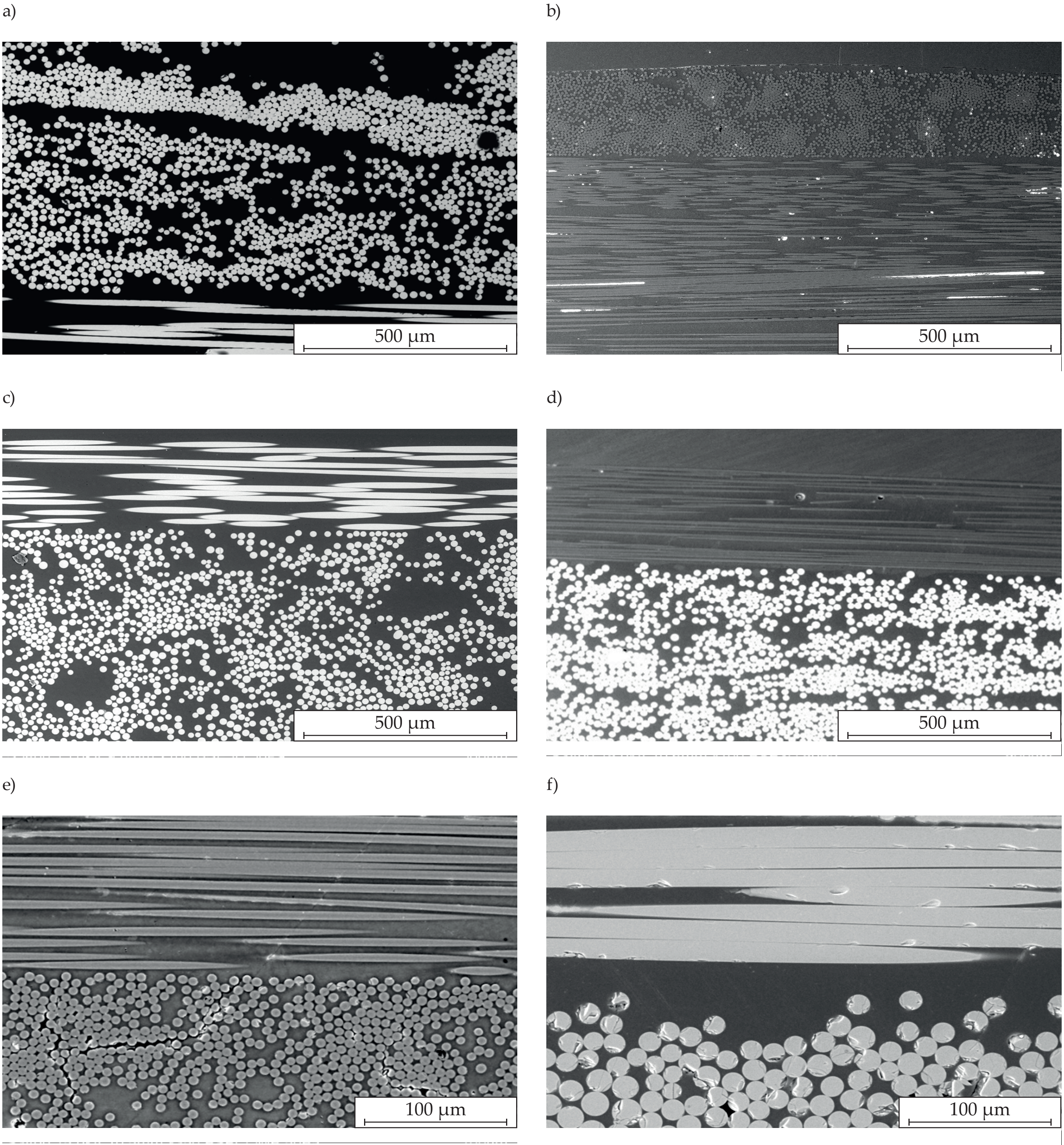

Fig. 5. SEM images of the composites: a) PPGF, b) PA6CF, c) PA66GF, d) PA6CFGF, e) PA66CF, f) PA6GF

modulus. Focusing on the local stiffness, the appropriate interphase size can be defined by the width of the cross-sectional area of the interphase surface. The measurements of the composite-coating interface width indicate that, among the coatings used, the varnish has a better interaction with the composite (Table 5). In the case of the film, the width of the interphase boundary does not exceed 18 nm, while for the details covered with polyurethane varnish, the composites made of PA66 have the largest width of the interphase region.

Based on the obtained phase difference and surface topography images, the surface roughness of the laminates was quantitatively determined by measuring the parameters R_a, R_z, R_{max} and R_q (Fig. 7). The measurements show that these parameters are low, which indicates that their surfaces are smooth (Table 6). The samples are characterized by gloss values measured in the 60° geometry in the range of 32.6–448 GU, which, according to the technical requirements of the Qualicoat quality mark for paints, varnishes and coatings, allows them to be classified as

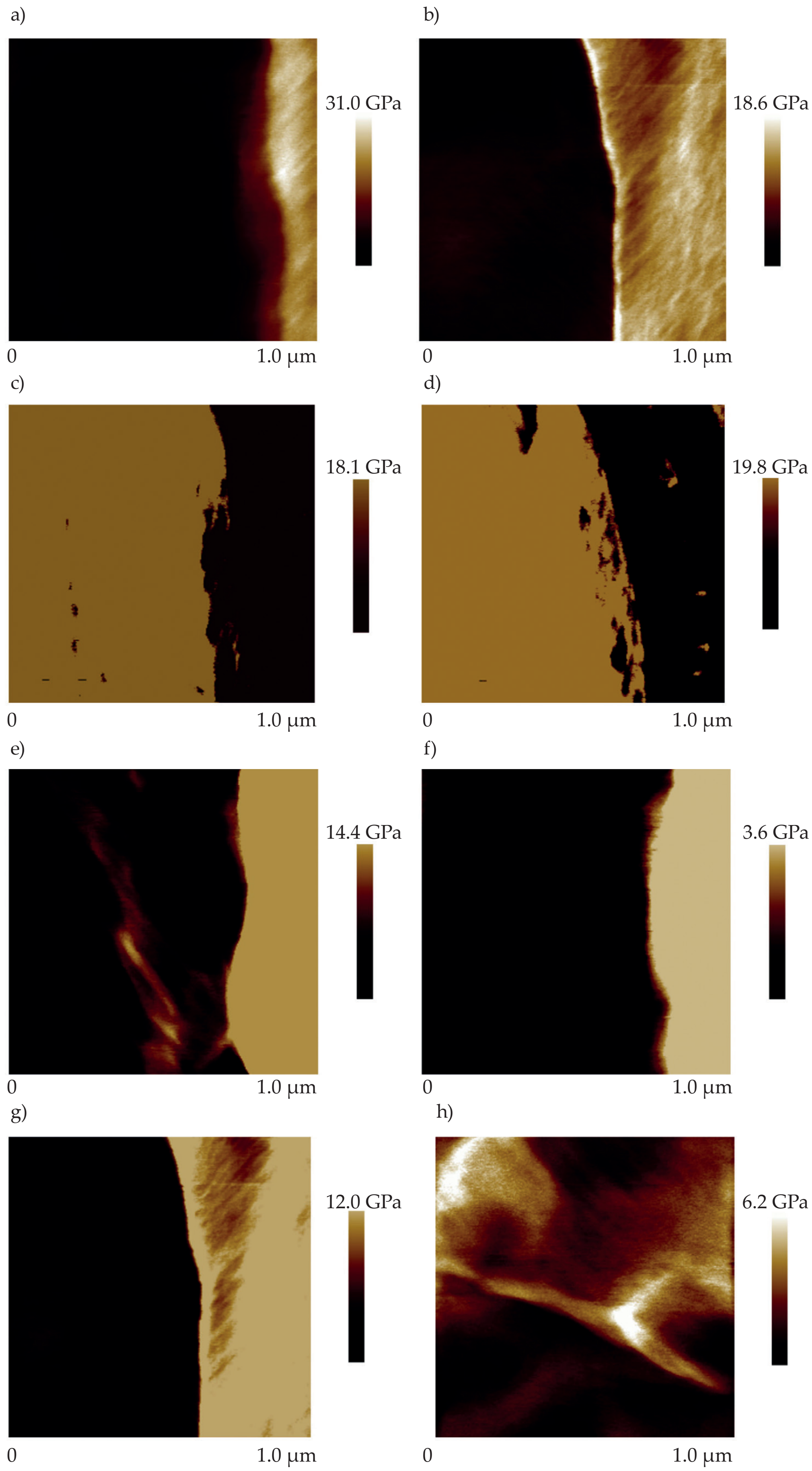

Fig. 6. Photos of the DMT modulus on the cross-sectional surface at the interface between the composite and the coating for the workpiece: a) PA66+PA66GF+PUR, b) PA66+PA66CF+PUR, c) PA6+PA6GF+PUR, d) PA6+PA6CF+PUR, e) PP+PPGF+PUR, f) PA66+PA66GF+film, g) PA6+PA6CF+film, h) PA6+PA6GF+film II

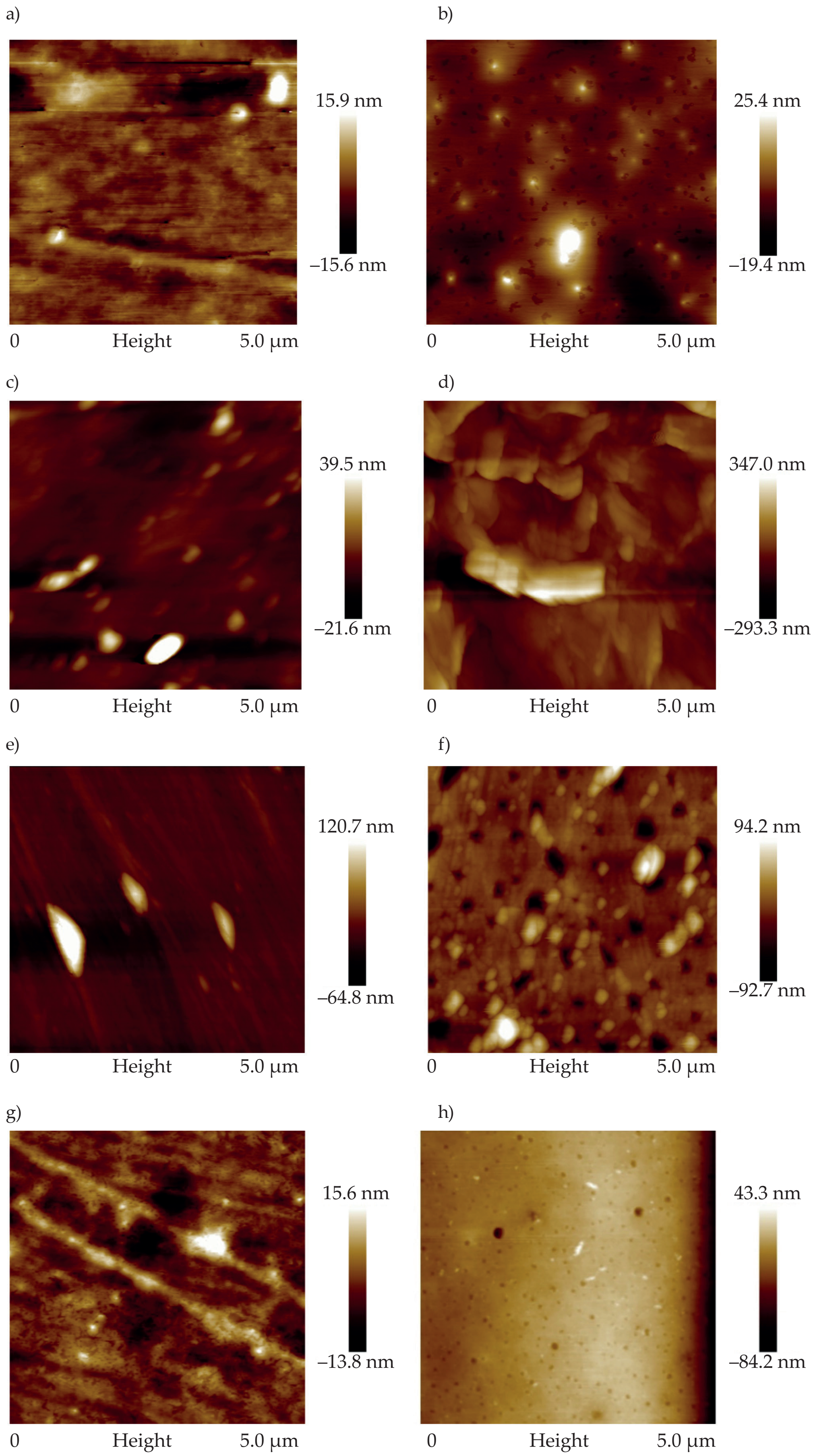

Fig. 7. Surface topography: a) PA6+PA6CF+PUR, b) PA6+PA6CF+film, c) PA6+PA6GF+PUR, d) PA6+PA6GF+film II, e) PA66+PA66CF+PUR, f) PA66+PA66GF+PUR, g) PA66+PA66GF+film, h) PP+PPGF+PUR

T a b l e 6. Surface nano-roughness and gloss values

Symbol	R_q	R_a	R_{max}	R_z	Gloss		
					20°	60°	85°
PA66+PA66GF+PUR	22.4	13.7	354	38.7	61.7	83.8	90.3
PA66+PA66CF+PUR	8.46	5.80	230	8.01	61.2	82.2	87.3
PA6+PA6GF+PUR	6.32	4.52	146	17.0	17.5	57.8	64.2
PA6+PA6CF+PUR	10.1	6.93	262	9.29	47.1	71.6	90.1
PP+PPGF+PUR	11.2	6.19	369	8.69	29.9	70.5	73.8
PA66+PA66GF+film	12.9	8.76	247	8.62	391.3	362.0	98.3
PA6+PA6CF+film	23.6	14.4	485	21.0	134.9	181.2	51.7
PA6+PA6GF+film II	124.0	86.6	1664	121	4.9	32.6	3.9

R_a – arithmetic mean deviation of the profile from the mean line, R_z – roughness height according to ten profile points, R_q – root means square deviation of the roughness profile, R_{max} – the highest value of the profile height Rz among the values occurring in the measuring section

characterized by semi-gloss (satin gloss) or gloss (satin – in the range of 31–70±7 GU, gloss – from 71±10 GU). The highest gloss values (above 100 GU) were recorded for samples finished with a film with a metallic effect. The lowest gloss is characteristic of PA6+PA6GF+PUR and PP+PPGF+PUR laminates, which is the result of greater surface roughness.

CONCLUSIONS

An innovative method of producing polymer elements with improved mechanical properties has been developed. Better visual qualities have also been achieved (smooth surface, uniform colour, better design), which is important in industries such as automotive, electronics and design. The developed technology enables faster, more energy-efficient production of polymer parts using modern, environmentally friendly materials that can be easily recycled, which will reduce the negative impact on ecosystems and increase the company's competitiveness. Thanks to the developed technology, the company will be able to offer more advanced and attractive products, which will allow it to stand out on the market and increase its competitiveness in the industry. The implementation of the project will allow the creation of a new quality range of polymer products that will be more durable, more aesthetic and ecological, which will benefit both the company and its customers.

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Authors contribution
T.S. – conceptualization, formal analysis; M.S. – conceptualization, formal analysis; A.S.-Z. – conceptualization, formal analysis; H.M. – methodology, investigation, formal analysis; M.Z. – methodology, investigation, formal analysis; K.B. – methodology, investigation, writing-original draft, visualization, writing-review and editing; R.O. – methodology, investigation, writing-original draft, visualization, writing-review and editing; M.O. – methodology, investigation, writing-original draft; G.B. – methodology, investigation, writing-original draft; M.S. – conceptualization, formal analysis.

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Conflict of interest
The authors declare no conflict of interest.

REFERENCES

[1] Rabek J.F.: „*Polimery i ich zastosowania interdyscyplinarne*" 1st edition, Wydawnictwo Naukowe PWN, Warsaw 2020.
[2] Phiri R., Rangappa S.M., Siengchin S. *et al.*: *Heliyon* **2024**, *10(21)*, e39611. https://doi.org/10.1016/j.heliyon.2024.e39661
[3] Rubio E.M., Blanco D., Marín M.M. *et al.*: *Procedia Manufacturing* **2019**, *41*, 1047. https://doi.org/10.1016/j.promfg.2019.10.032
[4] Sharma S., Sudhakara P., Nijjar S. *et al.*: *Materials Today: Proceedings* **2018**, *5(14, Part 2)*, 28195. https://doi.org/10.1016/j.matpr.2018.10.063
[5] Dai D., Fan M.: "Wood fibres as reinforcements in natural fiber composites: structure, properties, processing and applications" in "Natural Fibre Composites" (edit. Hodzic A., Shanks R.), Woodhead Publishing, Cambridge 2014, p. 3.

https://doi.org/10.1533/9780857099228.1.3
[6] Hsissou R., Seghiri R., Benzekri Z. *et al*.: *Composite Structures* **2021**, *262*, 113640. https://doi.org/10.1016/j.compstruct.2021.113640
[7] Sharma A.K., Bhandari R., Aherwar A. *et al*.: *Materials Today: Proceedings* **2020**, *21(3)*, 1559. https://doi.org/10.1016/j.matpr.2019.11.086
[8] Dang Z.M., Yuan J.K., Zha J.W. *et al*.: *Progress in Materials Science* **2012**, *57(4)*, 660. https://doi.org/10.1016/j.pmatsci.2011.08.001
[9] Alamry A.; *Journal of Engineering Research*, in-press, available online 21 September 2024. https://doi.org/10.1016/j.jer.2024.09.006
[10] Khan F., Hossain N., Mim J.J. *et al*.: Journal of Engineering Research, in-press, available online 27 February 2024. https://doi.org/10.1016/j.jer.2024.02.017
[11] Szederkenyi B., Kovacs N.K., Czigany T.: *Advanced Industrial and Engineering Polymer Research* **2025**, *8(1)*, 113. https://doi.org/10.1016/j.aiepr.2024.05.002
[12] Khalid M.Y., Rashid A.A., Al Arif A. *et al*.: *Results in Engineering* **2021**, *11*, 100263. https://doi.org/10.1016/j.rineng.2021.100263
[13] Mahesh V., Joladarashi S., Kulkarni S.M.: *Defence Technology* **2021**, *17(1)*, 257. https://doi.org/10.1016/j.dt.2020.04.002

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