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Piotr Olesik*, Mateusz Kozioł, Jakub Jała

Silesian University of Technology, Faculty of Materials Engineering, ul. Z. Krasińskiego 8, 40-019 Katowice, Poland
**Corresponding author. E-mail: Piotr.Olesik@polsl.pl*

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PROCESSING AND STRUCTURE OF HDPE/GLASSY CARBON COMPOSITE SUITABLE FOR 3D PRINTING

The following paper discusses the studies of high-density polyethylene (HDPE) reinforced with glassy carbon (GC) particles. The conducted research focused on the processing properties of the material. Samples were made from extruded HDPE filament reinforced with GC. The granulate for extrusion was made by depositing GC particles on the surface of HDPE granules in ethylene alcohol. The granulate was subsequently extruded in the form of a filament (1.6 mm in diameter). The filament was cut into smaller pieces, which were then prepared and examined using a light microscope. Density measurements and quantitative analysis were performed to examine the amount of glassy carbon in the samples. The measurements showed about a 1% volume of glassy carbon in the reinforced filament. The melt flow index was measured for the HDPE filament and HDPE filament reinforced with GC. The viscosity curves for the neat HDPE and the composite filament were determined. The reinforced HDPE filament was characterized by slightly lower flow parameters; however, the difference between the results was insignificant for material processing. The maximum feed rate of the prepared filament for the FDM 3D printing process was evaluated by mathematical modeling. The results show that both the prepared materials have a similar printing capability as commonly used PLA, only the composite filament should have a 1.4% lower feed rate than the neat HDPE.

Keywords: HDPE, glassy carbon, composite, extrusion, 3D printing, FDM technology

WŁAŚCIWOŚCI PRZETWÓRCZE I STRUKTURA KOMPOZYTÓW HDPE/WĘGIEL SZKLISTY PRZEZNACZONYCH DO DRUKU 3D

Przedstawiona praca dotyczy wstępnych badań nad polietylenem wysokiej gęstości (HDPE) zbrojonym cząstkami węgla szklistego (GC). Przeprowadzone badania skupiały się wokół struktury oraz właściwości przetwórczych uzyskanego kompozytu. Próbki zostały wytworzone z wytłoczonego filamentu HDPE zawierającego węgiel szklisty. Granulat do wytłaczania został przygotowany poprzez osadzanie cząstek GC na powierzchni granul HDPE w alkoholu etylowym, a następnie po wysuszeniu wytłoczony w postaci filamentu o średnicy ok. 1,6 mm. Przygotowany filament został poddany regranulacji, a następnie poddany obserwacji na mikroskopie świetlnym. Za pomocą pomiarów gęstości oraz analizy obrazu zdjęć z mikroskopu oceniono udział węgla szklistego w osnowie HDPE. Pomiary wykazała udział objętościowy zbrojenia na poziomie 1%. Właściwości przetwórcze zostały ocenione poprzez pomiary MFI oraz wyznaczonych na ich podstawie krzywych lepkości. Kompozytowy filament wykazywał nieznacznie mniejsze płynięcie w porównaniu do bazowego tworzywa. Ostatecznie oceniono maksymalny feed rate w procesie drukowania 3D (FDM) za pomocą modeli analitycznych dla wytworzonych filamentów. Wyniki modelowania pokazują, że oba przygotowane materiały mógłby być drukowane przy podobnych prędkościach jak popularne PLA.

Słowa kluczowe: HDPE, węgiel szklisty, kompozyty, wytłaczanie, druk 3D, FDM

INTRODUCTION

Carbon reinforced composites are efficiently used in various applications. One of most interesting groups is thermoplastic composites, especially high-density polyethylene (HDPE) based ones. This is particularly important because of the necessity to utilize large amounts of recycled polyethylene in a short time [1-3]. Carbon fillers can enhance the numerous properties of neat HDPE such as wear resistance, electrical conductivity, thermal conductivity or even the mechanical properties [4-7]. There are different forms of carbon that have been considered as a filler to date. In scientific reports information can be found about using carbon nanotubes (multi- or single-wall) [6, 8-10], carbon fibers [7, 11], graphite (micro- or nanopellets) [12,13], nanodiamonds [14] or graphene [10, 15]. The research conducted to date has shown that HDPE as the matrix can support the unique properties of carbon and effectively be used as a biomaterial, insulator or bearing. However, there has been no declared case of using glassy carbon as a reinforcement for HDPE composites.

Glassy carbon (GC), as a non-graphitized and non-graphitizable form of carbon, has been successfully used as the reinforcing phase in numerous composite materials. In the form of foams, it has been used as the

skeleton reinforcement for aluminum [16, 17] and magnesium [18, 19] matrix composites. In both cases, GC improved the wear resistance of the neat material. Similar behavior was seen in epoxy-based composites with GC particles – an instance is study [20]. The prepared material not only had enhanced wear resistance but was also much stiffer. Another example of an epoxy-GC composite application is wear resistant coatings. For instance, using epoxy resin containing GC particles causes stabilization of the coefficient of friction in the case of combustion engine push rods made of 17HNM steel [21, 22]. The described works have shown that using GC as a reinforcing filler can be highly beneficial.

In this work, the influence of GC particles on the processing properties such as MFI and viscosity were examined. Furthermore, the structure of the HDPE/GC composite material formed as a filament was investigated in terms of the distribution of particles in the polymer matrix and the volume fraction. In addition, prediction of the 3D printing feed rate for assumed standard process conditions was performed in order to evaluate the applicability of the composite for this technique.

MATERIALS AND METHODS

As the matrix for the composite filament, HDPE Hivorex 2600J (by Lotte Chemical, South Korea) was used. The reinforcing GC particles in the form of powder were prepared by high-energy ball milling from glassy carbon made by prof. Jerzy Myalski (Silesian University of Technology, Faculty of Materials Engineering, Poland). The obtained micrometric powder (D_{50} = 3 μm; D_{90} = 10 μm) was first deagglomerated in an ultrasonic bath for 15 minutes in ethylene alcohol and then mixed with HDPE granulate in an ultrasonic bath for a subsequent 15 minutes. The mixture was held at 60°C for one day until the alcohol evaporated. The prepared granulate of HDPE covered with a GC layer and neat HDPE granulate were dried and extruded with a ZAMAK DTR EHP-2x16S extruder (by Zamak, Poland) with a nozzle temperature of 160°C. The extruded mass was pulled and wound using an original self-constructed facility, enabling the formation of a homogeneous thin filament. The obtained filament had diameter of c.a. 1.6 mm.

To evaluate the effective content (volume fraction) of glassy carbon in the obtained composite, density measurement was made using the Archimedes method. The mean value was taken from eight filament samples and the test was carried out in 98% ethanol. The density of the glassy carbon powder used to prepare the composite was investigated by a pycnometer using three samples. The volume fraction of glassy carbon was calculated with Eq. (1):

$$\Phi_{gc} = 1 - \frac{\rho_{mGC} - \rho_{gc}}{\rho_{H0} - \rho_{gc}} \quad (1)$$

where: ρ_{mGC} – density of HDPE/GC composite [kg/m^3]; ρ_{gc} – density of glassy carbon; ρ_{H0} – density of neat HDPE.

Investigation of the composite structure was conducted using a GX71 Olympus light microscope (by Olympus, Japan). In order to confirm the volume fraction of GC in the HDPE matrix, quantitative analysis of the microstructure was performed using Met-Ilo software (developed by prof. Janusz Szala, Silesian University of Technology, Poland).

The melt flow index (MFI) was determined using a CEAST plastometer (by CEAST/Instron, USA). Cut pieces of filament were used as the sample. In order to analyze the shear-thinning behavior, the same CEAST plastometer was used. Measurements of the MFI values were carried out at five different loads at 190°C and three different temperatures at a 2200 g load. The collected data was used to calculate the shear rate (Eq. (2)) and viscosity (Eq. (3)):

$$\dot{\gamma} = \frac{4MFI}{600\rho\pi R_N^3} \quad (2)$$

where: ρ – melt density [kg/m^3]; MFI – melt flow index [g/10 min]; R_N – nozzle radius [m].

$$\eta = \frac{75\rho R_N^4 Lg}{MFIR_p^2 l} \quad (3)$$

where: L – load [kg]; g – gravitational acceleration [m/s^2]; R_p – pistol radius [m]; l – nozzle length [m].

RESULTS AND DISCUSSION

Composite structure

The density of the filament samples measured by the Archimedes method was 0.952±0.001 for the neat HDPE and 0.961±0.004 for the HDPE/GC composite, where the density of the glassy carbon powder was calculated as 1.777±0.002. The obtained density values were then used to calculate the volume fraction of GC particles in the composite (Φ_{gc}), which was 1.2%.

The microstructure of the obtained composite filament is shown in Figure 1. The white particles interpreted as GC are evenly distributed in the HDPE matrix and no agglomerates were observed. Quantitative analysis revealed GC volume fraction Φ_{gc} = 0.965%, which is in good agreement with the density calculations (Φ_{gc} = 1.2%). The difference between these two values can be explained by some minor impurities or a different crystallinity degree that could affect the density measurement. Moreover, some small particles of GC might not have been visible in the micrographs and have not taken part in the image analysis. The mean distance between the particles in the matrix was calculated as 4.07 μm, which is only c.a. 1 micrometer higher than the D_{50} of the added powder. This confirmed the observation about the homogenic distribution of the reinforcement in the polymer matrix.

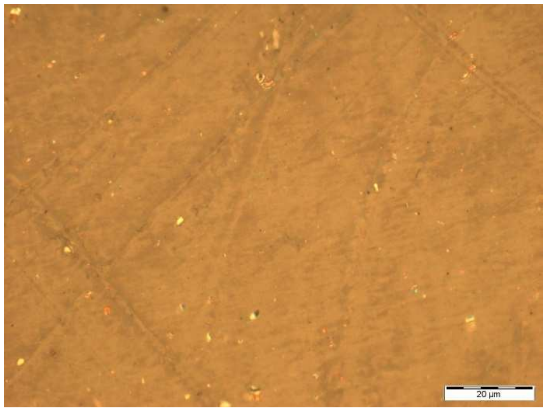

Fig. 1. Composite filament structure – light microscope

Rys. 1. Struktura filamentu kompozytowego – mikroskop świetlny

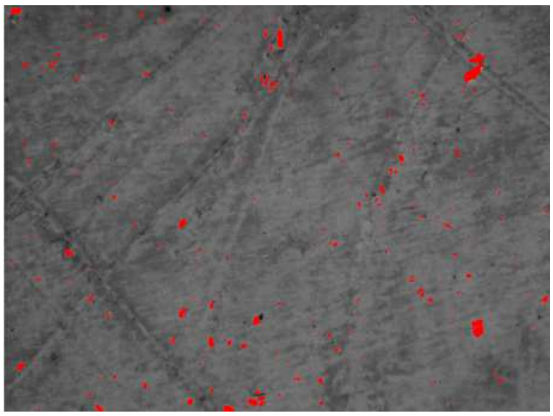

Fig. 2. Detected glassy-carbon (GC) particles – micrograph analysis using Met-Ilo software

Rys. 2. Detekcja cząstek węgla szklistego za pomocą Met-Ilo

Determination of viscosity curves

The results of the MFI measurements are presented in Figures 3 and 4. As expected, the addition of GC decreased the polymer flow. Nonetheless, the differences between the samples are relatively small, which should result in a negligible difference in the processing of these materials.

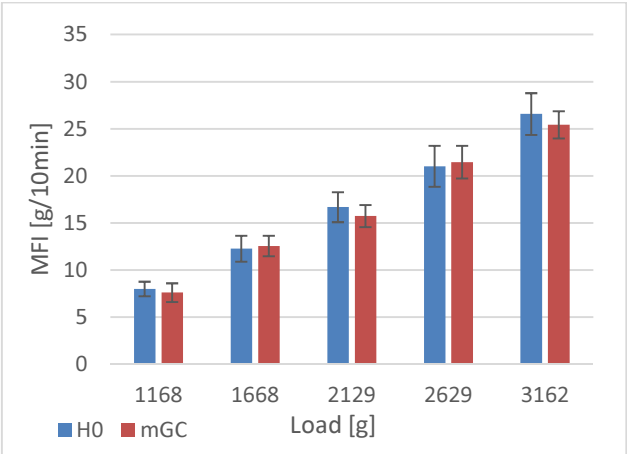

Fig. 3. Melt flow index results for different loads at 190°C: H0 – neat HDPE, mGC – HDPE/GC composite

Rys. 3. Wyniki MFI przy różnym obciążeniu w temperaturze 190°C: H0 – czysty HDPE, mGC – HDPE/GC kompozyt

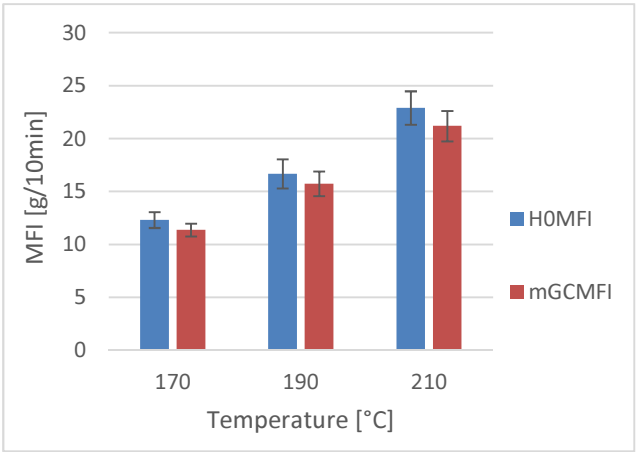

Fig. 4. Melt flow index result for different temperatures at 2129 g load: H0 – neat HDPE, mGC – HDPE/GC composite

Rys. 4. Wyniki MFI przy różnych temperaturach pod obciążeniem 2129 g: H0 – czysty HDPE, mGC – HDPE/GC kompozyt

To estimate the shear rate and hence viscosity, *MFI* needs to be converted into a flow rate – Q [m^3/s]. To do so a melt density is needed. According to other authors [11, 23] the melt density can be assumed as 80% of the solid density and was stated at 0.754 g/cm^3 for the neat HDPE and 0.767 g/cm^3 for the HDPE/GC. The viscosity curves are shown in Figures 5 and 6.

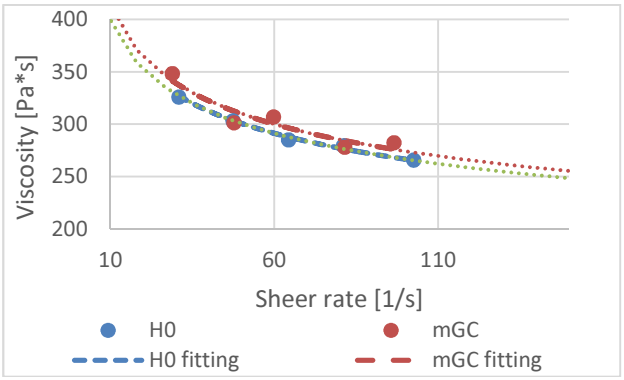

Fig. 5. Viscosity vs sheer rate curve with fitting curves

Rys. 5. Krzywe lepkości w funkcji prędkości ścinania: H0 – czysty HDPE, mGC – HDPE/GC kompozyt

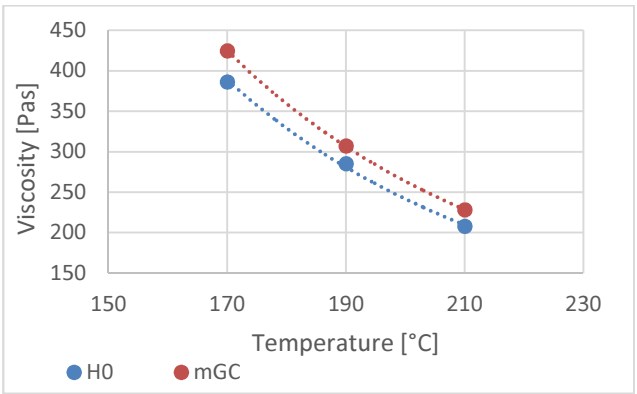

Fig. 6. Viscosity vs temperature curve: H0 – neat HDPE, mGC – HDPE/GC composite

Rys. 6. Krzywe lepkości w funkcji temperatury: H0 – czysty HDPE, mGC – HDPE/GC kompozyt

The fitting curves were obtained in Origin 2019 software using a power-law equation (Eq. (4)) and the R^2 value was 0.998 and 0.966 for the neat HPDE and the HDPE/GC respectively. Similarly, as in the *MFI* results only a slight difference between the samples was observed – the addition of GC resulted in an increase in the melt viscosity. Temperature dependence α was obtained by optimizing Eq. (5) using the Solver expansion in Microsoft Excel. The parameters of the fitted curves are listed in Table 1.

$$\eta = K\langle\dot{\gamma}\rangle^{n-1} \tag{4}$$

where: K – consistency index [Pa · s^n]; n – power law index.

$$\eta = Ke^{-\alpha(T-T_{ref})}\langle\dot{\gamma}\rangle^{n-1} \tag{5}$$

where: T_{ref} – temperature at reference viscosity (190°C) [°C]; α – temperature dependence coefficient [1/°C].

TABLE 1. **Fitting parameters of viscosity curves: H0 – neat HDPE, mGC – HDPE/GC composite**
TABELA 1. **Parametry dopasowania dla krzywych lepkości: H0 – czysty HDPE, mGC – HDPE/GC kompozyty**

Parameters	H0	mGC
K	593.140	618.108
n	0.826	0.824
α	0.012	0.014

Predicting maximum filament feed rate in 3D printing for HDPE/GC composite

In order to predict the usage of the obtained composite filaments for 3D printing (by FDM – the fused deposition modeling method), the model proposed by Serdeczny et. al [24] was used (Eq. (6)). The mentioned authors consider that the filament should be sufficiently heated in the barrel section of the FDM printer (Fig. 7) to be extruded properly

$$V_{max} = \frac{h\Delta T\pi D_b L_b}{[\lambda + C_m(T_{out} - T_{in})]\rho_m A_f} \tag{6}$$

where: h – heat transfer coefficient [W/m^{2}K]; ΔT – mean logarithmic temperature difference [K]; D_b – barrel section diameter [m]; L_b – barrel section length [m]; λ – heat of fusion [J/kg]; C_m – heat capacity of melt [J/kgK]; A_f – filament cross-section area [m^2]; T_{out} – extruded filament temperature [K]; T_{in} – initial filament temperature [K].

$$\Delta T = \frac{(T_m - T_{in}) - (T_m - T_{out})}{\ln\frac{T_m - T_{in}}{T_m - T_{out}}} \tag{7}$$

where T_m – filament melting point [K].

Other authors use the maximum feed rate (V_{max}) as the filament speed at which grinding or buckling at the rollers occur [26, 27]. Nonetheless, analysis of the feeding force shows that filament extrusion starts disrupting earlier than filament failure [24, 25, 28]. Therefore, the mathematical model proposed by Serdeczny et. al seems a better option to predict the material usage for 3D printing because it considers filament melting as crucial for the FDM process.

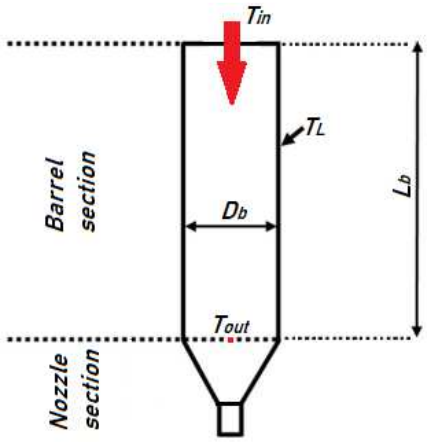

Fig. 7. Diagram of liquefier – part of FDM printer
Rys. 7. Schemat głowicy do druku FDM

To estimate V_{max} some assumptions were needed. Predicting the V_{max} value in this study was made for an E3D v6 hot-end, filament diameter 1.75 mm and nozzle diameter 0.4 mm. In work [1], the authors of the model adjusted the value of the heat transfer coefficient to match the experimental feed rates measurements for PLA. Similarly, in our prediction the value of h = 228 W/m^{2}K was taken. Thermal factors such as the heat of fusion and heat capacity were also assumed. Using the density result, the heat of fusion was established as $\lambda = \lambda_0 \cdot w_c$, where λ_0 is the heat of fusing fully crystalline HDPE and w_c is the weight fraction of the crystalline phase [29, 30]. Different values of heat capacity were used for the HDPE and HDPE/GC samples. For the composite C_m was estimated as the linear function of the heat capacity of the components and their weight fractions. All the employed values are listed in Table 2. The results of predicting the maximum feed rate are shown as a function of the liquefier temperature in Figure 8.

TABLE 2. **Assumed parameters for analytical feed rate prediction for neat HDPE (H0) and HDPE/GC composite (mGC)**
TABELA 2. **Założone parametry do analitycznego przewidywania prędkości podawania filamentu**

	h [W/m^{2}K]	D_b [m]	L_b [m]	λ [J/kg]	C_p [J/kgK]	T_{out} [K]	T_{in} [K]	ρ_m [kg/m^3]
H0	228	0.0019	0.0115	203557	1900	453	363	754.63
mGC	228	0.0019	0.0115	203557	1890	453	363	766.83

The maximum feed rate obtained in the prediction for the HDPE/GC composite and for the neat HDPE is comparable to materials commonly used for FDM printing (PLA, ABS) [24, 25]. It testifies that the obtained HDPE/GC composite is probably suitable material for FDM technology.

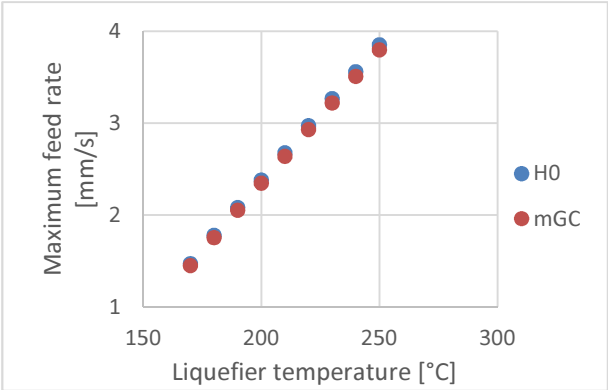

Fig. 8. Prediction of filament maximum feed rate for neat HDPE (H0) and HDPE/GC composite (mGC)

Rys. 8. Przewidywana maksymalna prędkość podawania filamentu dla czystego HDPE oraz kompozytu HDPE/GC

CONCLUSIONS

- Depositing micrometric glassy carbon powder on polymer granules resulted in a c.a. 1% particle volume fraction in the matrix. The presented method of preparing a composite of HDPE with glassy carbon particles proved to be efficient; it resulted in homogeneous distribution of the reinforcing particles in the polymer matrix.
- The presented composite material has similar processing properties to neat HDPE.
- The predicted maximum feed rate for the HDPE-glassy carbon composite and for the neat HDPE is comparable to materials already used for 3D printing.
- The model applied to predict the feed rate needs to be verified experimentally in future work; it neglects part of the processing effects affecting the filament in the printer nozzle, which must be taken into account to improve the precision of the final results.

Acknowledgements

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