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EXAMINATIONS OF STRUCTURE AND PROPERTIES OF POLYMER COMPOSITE WITH GLASS FIBER

The article discusses the results of research on the structure and mechanical properties of polypropylene composites with glass fiber. The samples for the examinations were made using a Krauss-Maffei (KM65 – 160C1) screw injection molding machine. The investigations encompassed composites with a polypropylene matrix which contained 30 and 50% glass fiber (GF). Part of the material was processed by heat treatment in the form of annealing. The crystal structure of the samples was analyzed on a wide-angle X-ray diffractometer - Seifert 3003 T-T. In most of the obtained diffraction patterns a few strong diffraction reflexes can be seen. They were identified as reflections derived from polypropylene polymorphs: α (monoclinic), β (hexagonal) and from the smectic phase of polypropylene. Dynamic mechanical analysis (DMA) tests were performed on a DMA 242 Netzsch instrument under the mode of a 3-point bending clamp with an oscillatory frequency of 3.0 Hz. The transition to the glassy state is the most evident for polypropylene. In the case of polypropylene composites, the transition to the glassy state is less evident. The largest tendency of the storage modulus value as a function of temperature to decrease was noted for polypropylene and the smallest for the polypropylene composite with a 50% glass fiber content. Higher values of storage modulus E′ were noted after annealing. For all the samples, glass transition temperature T_g decreases after annealing. Investigations of the mechanical properties of the studied composites were also performed: tensile strength testing, Young's modulus, hardness and impact test. In each case the addition of glass fiber caused an increase in mechanical properties. Moreover, it can be noted that the values of the mechanical properties of PP/GF composites after annealing are higher than those of PP/GF composites before annealing. Both the Vicat softening temperature as well as heat deflection temperature are higher for the samples after annealing. SEM micrographs show the mechanism of breakage of the glass fibers and damage of the matrix material. During observation of the fractures, no significant fiber pullout from the polymer matrix was noted. This demonstrates the good adhesion of the glass fiber to the matrix.

Keywords: polymer composites, polypropylene, glass fiber, mechanical and thermal properties

BADANIA STRUKTURY I WŁAŚCIWOŚCI KOMPOZYTU POLIMEROWEGO Z NAPEŁNIACZEM WŁÓKNISTYM

Omówiono wyniki badań struktury i właściwości mechanicznych kompozytu polipropylenu z włóknem szklanym. Próbki do badań wykonano na wtryskarce ślimakowej Krauss - Maffei (KM65 - 160C1). Badaniom poddano kompozyty na osnowie polipropylenu, które zawierały 30 i 50% włókna szklanego. Część materiału poddano obróbce cieplnej polegającej na wygrzewaniu. Strukturę krystaliczną próbek analizowano na dyfraktometrze rentgenowskim Seifert 3003 T-T. Na większości otrzymanych dyfraktogramach można zaobserwować kilka silnych refleksów dyfrakcyjnych. Zidentyfikowano je jako refleksy pochodzące od odmian polimorficznych polipropylenu: α (jednoskośna), β (heksagonalna) oraz fazy smektycznej polipropylenu. Dynamiczne właściwości mechaniczne kompozytów na osnowie polipropylenu badano na aparacie do badań dynamicznych DMA 242 firmy Netzsch. Przejście w stan szklisty jest najbardziej widoczne dla polipropylenu. W przypadku kompozytów polipropylenu przejście w stan szklisty jest mniej widoczne. Największą tendencję obniżenia wartości modułu zachowawczego w funkcji temperatury odnotowano w przypadku polipropylenu, a najmniejszą w przypadku kompozytu polipropylenu zawierającego 50% włókna szklanego. Po wygrzewaniu zauważono wyższe wartości modułu zachowawczego. Dla wszystkich próbek zarejestrowano obniżenie wartości temperatury zeszklenia T_g po wygrzewaniu. Wykonano również badania właściwości mechanicznych: wytrzymałość na rozciąganie, moduł Younga, twardość i udarność. W każdym przypadku wraz ze wzrostem zawartości włókna szklanego w kompozycie wzrastają własności mechaniczne. Ponadto, wygrzewanie prowadzi do uzyskania korzystniejszych właściwości mechanicznych badanych kompozytów. Zarówno temperatura mięknienia wg Vicata, jak i wartości temperatury pod obciążeniem (HDT) są wyższe dla próbek po wygrzewaniu. Mikrofotografie SEM przedstawiają mechanizm uszkodzenia włókien szklanych oraz materiału osnowy. Podczas obserwacji przełomów nie zauważono znaczącego wyciągania włókien z polimerowej osnowy. Świadczy to o dobrej adhezji włókien szklanych z polimerową osnową.

Słowa kluczowe: kompozyty polimerowe, polipropylen, włókno szklane, właściwości mechaniczne i cieplne

INTRODUCTION

Polypropylene and its composites are widely used in many engineering applications as alternate products for metal-based ones. In recent years, polymer matrix composites reinforced with glass fiber have become a promising research area for the development of advanced engineering materials. In earlier days, polyolefins were used only for packaging applications which demand only moderate mechanical properties [1]. However, in recent times polypropylene (PP) has emerged as the most widely used commodity plastic in the automobile, electronic and domestic appliance industries [2, 3]. Polypropylene, as a traditional thermoplastic, has been widely used in everyday life and industry due to its excellent heat resistance, good dimensional stability, processing properties, non-toxicity, and low price. Nevertheless, polypropylene still needs mechanical improvement to expand its applications as structural plastics. Fiber reinforced polypropylene is one of the most popular ways to solve this problem [1-6]. Glass fibers in composites provide the combined benefits of individual fillers like high performance, long life and light weight characteristics, and at the same time mitigate their undesirable properties. It has been found that the properties of glass fiber reinforced polymer composites mainly depend on the following factors: (1) the content of fiber, (2) the interaction between the fiber and matrix, (3) the aspect ratio of the fiber, and (4) the properties of the matrix [4-6]. The technical and economic utility of polymeric composites depend on whether they meet rigidity and durability requirements in order for their functional life to be sufficient. Composite properties are also affected by the durability and thermal properties of the filler, matrix rigidity and the durability of the bond between the filler and matrix. Injection molding processes are frequently employed to make polymer composites with glass fiber [7-9]. In general, a high glass fiber content is required in order to obtain high strength composites. Therefore, the effect of the fiber content on the structure and mechanical properties of polymer composites is of particular interest and significance. It is often observed that an increase in the fiber content leads to an increase in the strength and modulus [10, 11]. The properties of polymeric molded pieces can be improved by using heat treatment that allows the degree of crystallinity to be increased. A higher degree of crystallinity positively affects changes in the mechanical, thermal and functional properties of products [7, 12]. In designing composite parts (e.g. automotive body components), precise knowledge of the thermomechanical behavior is also needed as these parts are usually subjected to a broad range of temperatures either during assembly or in-service. The aim of the study was to analyze the crystal structure, mechanical and thermal properties of polypropylene composites with glass fiber prior to and after the annealing process.

MATERIALS AND EXPERIMENTAL PROCEDURE

This work presents the results of investigations on composites made of granulates by Polimarky (Rzeszow, Poland). These granulates contained polypropylene - Malen P J - 400 produced by Petrochemia Płock and E-glass fibers. Glass fibers with a final length of 6 mm were covered with a silane preparation. Samples for the investigations were prepared by means of injection with a Krauss-Maffei injection machine (KM65 - 160C1). The investigations encompassed composites with a polypropylene matrix which contained 30 and 50% glass fiber (GF). For comparison purposes the matrix material was also tested. Part of the material was processed by heat treatment in the form of annealing at the temperature of 130°C in air. The annealing rate amounted to 0.015°C/s, annealing time 900 s per mm of sample thickness, cooling rate 0.010°C/s. The designations of individual specimens and the percentage of glass fiber content are presented in Table 1.

TABLE 1. **Designations of specimens used in study**
TABELA 1. **Oznaczenie próbek do badań**

No.	Specimen "a" - samples after annealing	Glass fiber content [%]
1.	PP	-
2.	PP-a	-
3.	PP70/GF30	30
4.	PP70/GF30-a	30
5.	PP50/GF50	50
6.	PP50/GF50-a	50

The crystal structure of the samples was analyzed by means of a wide-angle X-ray diffractometer - Seifert 3003 T-T. The filtered radiation of a copper anode lamp, $\lambda = 0.154$ nm was applied. The stepped method of measurement within the range of scattering angles of 2θ from 5° to 60° with a step of 0.1° was used. Dynamic mechanical analysis (DMA) tests were performed on a DMA 242 Netzsch instrument under the mode of a 3-point bending clamp with an oscillatory frequency of 3.0 Hz. Temperature scans were recorded from −25°C to 130°C at the heating rate of 5°C/min. Static tensile testing was carried out using a Zwick tensile testing machine. Specific samples were used for the test in accordance with the PN EN ISO 527-3:1998 standard. During the tensile test the longitudinal elasticity coefficient (Young's modulus) was also determined. Young's modulus is the ratio of stress to the corresponding strain of the material below the proportionality limit (according to Hooke's law). Sample elongation in the proportionality range was recorded using a universal extensometer: MTS 634.31F-24. The hardness test was carried out by the ball cavity method with a total load of 358 N. The Charpy impact test was carried out as per the ASTM D 6110-97 standard to measure the impact strength. Investigations of the thermal properties of the tested composites were conducted by determining the Vicat softening temperature and the heat deflection temperature (HDT). A HAAKE N8 measuring device was used for the tests. A Hitachi S-4700 scanning electron microscope was used to examine the fracture surfaces of the PP/GF composites. Prior to scanning electron microscopy (SEM) observations, all the fracture surfaces of the tensile specimens were sputter-coated with gold.

INVESTIGATION RESULTS

The X-ray diffraction spectra of the polypropylene and composites prior to and after annealing are presented in Figure 1. In most of the obtained diffraction patterns a few strong diffraction reflexes can be seen. They were identified as reflections derived from polypropylene polymorphs: α (monoclinic), β (hexagonal) and from the smectic phase of polypropylene.

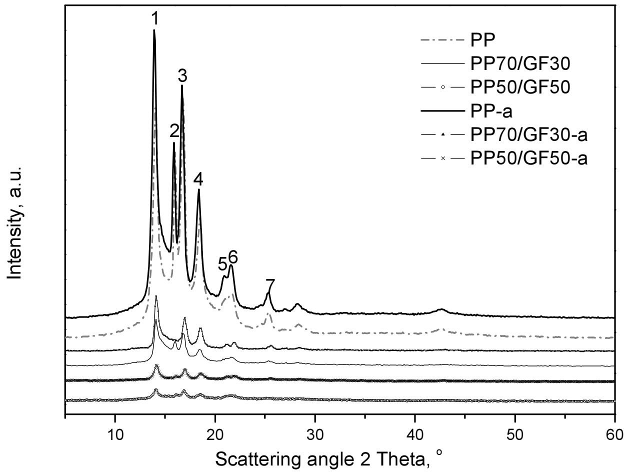

Fig.1. Diffraction curves for polypropylene and composites

Rys. 1. Krzywe dyfrakcyjne dla polipropylenu i kompozytów

Miller indices are marked at particular peaks. They are characteristic for isotactic polypropylene containing both α and β phase crystals [8, 9, 13-15]. The obtained values of the Miller indices for the investigated polypropylenes are collated in Table 2 together with the 2θ angle values.

TABLE 2. **Peak values obtained by XRD**

TABELA 2. **Wartości pików otrzymane metodą rentgenowską**

Sample	Placement - 2θ, ° Miller indicator (hkl)						
	1 α(110)	2 β(300)	3 α(040)	4 α(130)	5 α(110)	6 α(041)	7 α(060)
PP	14.03	16.00	16.75	18.49	21.02	21.63	25.34
PP-a	13.92	15.88	16.10	18.37	20.96	21.59	25.24
PP70/GF30	14.07	16.00	16.80	18.46	21.06	21.61	25.30
PP70/GF30-a	14.14	16.35	16.94	18.53	21.15	21.87	25.53
PP50/GF50	14.10	16.13	16.98	18.60	21.27	21.90	25.55
PP50/GF50-a	14.12	16.13	16.99	18.57	21.26	21.96	25.53

The Scherrer equation (1) was used to calculate the size of the crystallites. Crystallite sizes (D), were calculated in directions perpendicular to the lattice planes with Miller indices: (110), (040) and (130) for the α phase and (300) for the β phase. The calculated crystallite sizes for the polypropylene α and β phases are summarized in Table 3.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where D is the average crystallite size, λ is the wavelength of the X-ray radiations (Cu Kα radiation = = 0.154 nm), θ is the diffraction angle and β is the full width half maximum (FWHM). The concentration of the crystalline phase of polypropylene (i.e. crystallinity degree) was calculated in the form of the quotient of the total of integral intensities of crystalline reflexes to the integral intensity of diffraction curves. The results of these calculations are summarized in Table 3.

TABLE 3. **Size of crystallites D and degree of crystallinity of investigated samples determined by X-ray method**

TABELA 3. **Wielkości krystalitów i stopień krystaliczności badanych próbek wyznaczone metodą rentgenowską**

Sample	Size of crystallites, *D* [nm]				Degree of crystallinity [%]
	α (hkl)			β (hkl)	
	(110)	(040)	(130)	(300)	
PP	16.8	17.6	11.5	30.4	67.8
PP-a	18.5	19.1	13.2	28.4	73.7
PP70/GF30	21.5	14.6	8.6	13.8	53.0
PP70/GF30-a	22.2	15.6	13.5	12.3	70.0
PP50/GF50	22.0	9.6	16.1	13.5	32.8
PP50/GF50-a	17.1	14.7	10.5	19.1	43.4

The amorphous phase in the tested composites is a highly oriented smectic phase of polypropylene. The determined values of the size of the crystallites and the crystallinity degree (Table 3) should be treated as an estimation since due to the strong orientation of crystallites, the diffraction reflexes and maximums shapes are deformed compared to the literature values [13, 15]. Taking the abovementioned into consideration in comparison to the results of the investigations performed for the composite which contains 30% glass fiber after annealing, it should be observed that the very low intensity of the diffraction reflex which comes from the (300) plane it may be associated with orientation effects. Moreover, changes in the intensity of reflex (300) which come from the β form show that this form is less stable than the monoclinic type of α. As a result of annealing, significant changes occur in the structure of the tested composites. The size of matrix spherulites and the degree of crystallinity increase. After annealing the proportion of crystalline phases present in the polymer matrix increases. As a result of heating, the mobility of macromolecules increases and the fragmentation of existing crystal structures, mainly spherulites, occurs. These small pieces of crystal structures become new embryos. New spherulites form from embryos, mainly in the form of crystal plates (lamellas), and as a result of the ordering of some macromolecules of the amorphous phase. The growth of spherulites can occur through radial propagation evenly in all directions or through branches, starting from an embryo. Incorporating the glass fibers in the polymeric matrix caused adecrease in the crystallinity degree determined by the X-ray method (Table 3). This proves that glass fiber does not work as a factor which causes nucleation of the matrix crystallites. Figure 2 shows the storage modulus (*E′*) measured by DMA at 3 Hz as a function of temperature for polypropylene and its composites. The largest tendency of the storage modulus value as a function of temperature to decrease was noted for polypropylene and the smallest for the polypropylene composite with the 50% glass fiber content. Higher values of storage modulus *E′* were recorded for the samples after annealing.

Figure 3 exhibits plots of the mechanical loss factor (tanδ) as a function of temperature for various samples, and the glass transition temperatures (T_g) of the samples obtained from the plots are listed in Table 4.

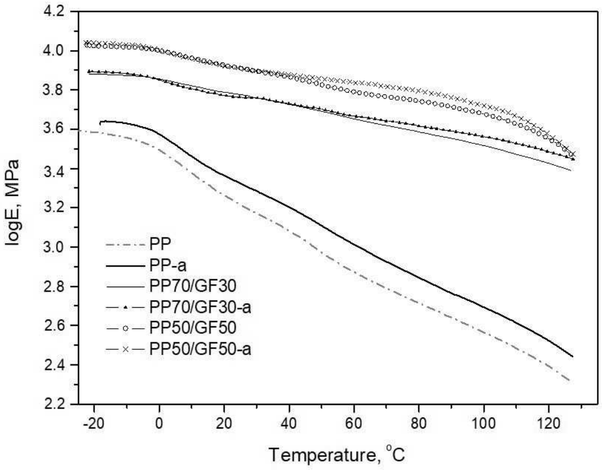

Fig. 2. Dependence of storage modulus (log*E*') as function of temperature at frequency of 3Hz

Rys. 2. Zależność modułu zachowawczego w funkcji temperatury przy częstotliwości 3 Hz

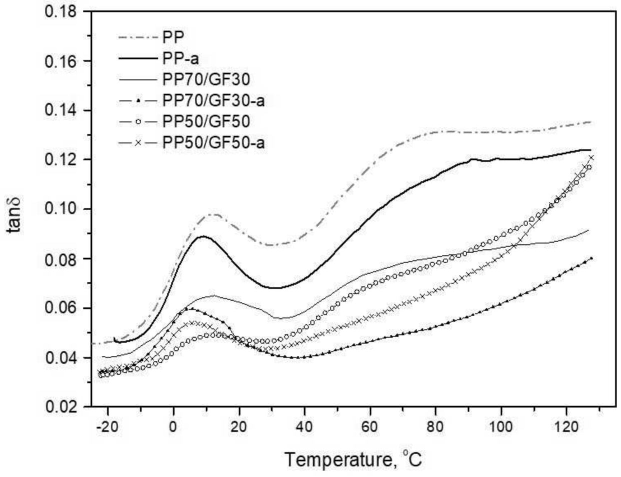

Fig. 3. Dependence of loss tangent coefficient (tan*δ*) as function of temperature at frequency of 3Hz

Rys. 3. Zależność współczynnika stratności mechanicznej (tan*δ*) w funkcji temperatury przy częstotliwości 3 Hz

TABLE 4. **Glass transition temperature (T_g) and tanδ peak of polypropylene and composites**

TABELA 4. **Temperatura przejścia w stan szklisty (T_g) i wartość współczynnika stratności mechanicznej tanδ dla polipropylenu i kompozytów**

Sample	T_g [°C]	tanδ peak at T_g
PP	11.50	0.098
PP-a	8.77	0.089
PP70/GF30	11.87	0.064
PP70/GF30-a	4.40	0.059
PP50/GF50	11.81	0.049
PP50/GF50-a	5.08	0.053

Two pronounced maxima can be clearly observed in the plots. The first maxima at the lower temperature is associated with β-relaxation resulting from the glass transition of PP (the peak temperature is T_g), while the other maximum at the higher temperature is related to the α-relaxation of PP. The origin of α-relaxation is associated with the intra-lamellar block-slip process in the crystalline phase or segment diffusion at the interface of the crystalline and amorphous phase [16]. As is clearly seen in Table 4, for all the samples T_g decreases after annealing. As for the decreased T_g, it could be a result of the decreased chain density in the amorphous phase after annealing [17].

Figure 4 shows the dependence between the stress and strain of the tested samples.

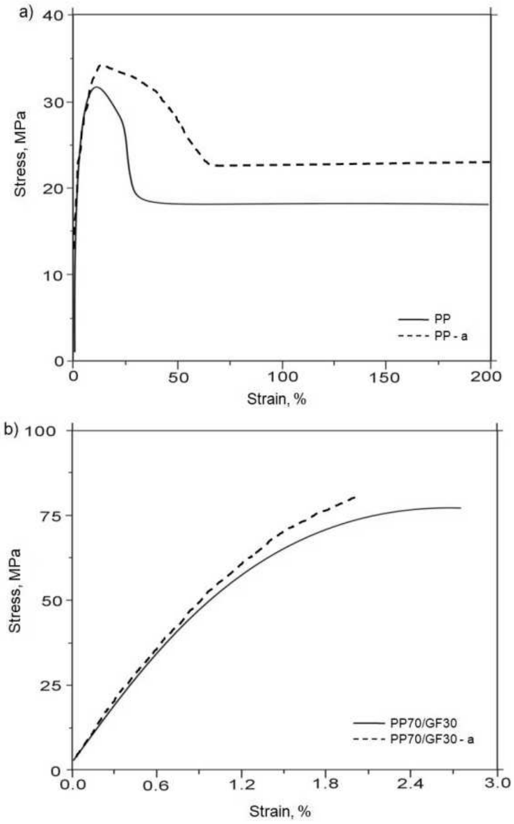

Fig. 4. Relations between stress and strain for tested samples: a) PP. b) composite PP70/GF30

Rys. 4. Zależności naprężenia od odkształcenia dla badanych próbek: a) PP, b) kompozyt: PP70/GF30

Figure 5 presents the results of the mechanical properties of the studied composites: tensile strength, Young's modulus, hardness and impact test.

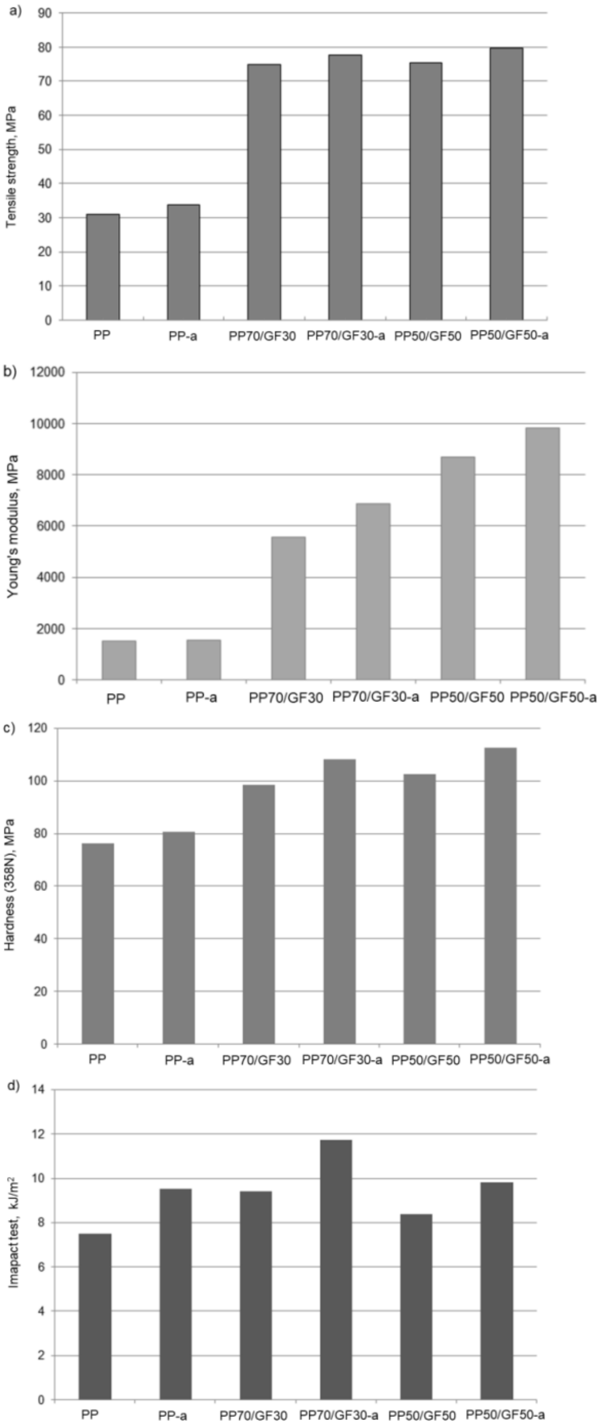

Fig. 5. Mechanical properties of studied composites: a) tensile strength, b) Young's modulus, c) hardness, d) impact test

Rys. 5. Własności mechaniczne badanych kompozytów: a) wytrzymałość na rozciąganie, b) moduł Younga, c) twardość, d) próba udarności

Static tensile strength testing (Fig. 5a) found the lowest value of tensile strength, an *Rm* of 31.07 MPa, for the polypropylene specimen. In each case, the addition of glass fiber caused an increase in tensile strength. The highest values were found for the specimens with additions of 30 and 50% glass fiber (74.76 and 75.26 MPa, respectively). The static tensile strength test demonstrated that annealing leads to an increase in tensile strength (Fig. 4). The highest tensile strength was observed for the PP50/GF50-a specimen (79.57 MPa). Glass fiber reinforced composites based on polypropylene are highly elastic materials: their Young's modulus is about 69000 MPa [18]. Therefore, the participation of glass fiber in the composite increases the elastic properties of the tested materials. The highest values of Young's modulus were observed for the PP50/GF50 specimens (8716 MPa for sample PP50/GF50 and 9842 MPa for sample PP50/GF50-a, respectively). Moreover, it can be noted from Figure 5b that the values of the Young's modulus of the PP/GF composites after annealing are higher than those of the PP/GF composites before annealing. Measurements using the ball indentation method used typically for composite and polymer materials were employed to provide a more comprehensive characterization of the mechanical properties of the composites obtained in the study. The data contained in Figure 5c show that the addition of glass fiber causes an increase in hardness. The mean hardness of polypropylene was 76.15 MPa. The additions of 30 and 50% of glass fiber caused an increase in hardness to 98.54 and 102.40 MPa. However, in each case the hardness of the samples after annealing is higher than the hardness before annealing. The highest hardness was observed for the PP50/GF50-a specimen (112.38 MPa). The Charpy impact strength of polypropylene and its composites are shown in Figure 5d. Glass fiber reinforced polypropylene composites are low impact resistance materials. During impact measurement, it was not possible to register the force and deflection of the sample. Analysis of the impact bending curves registered in the force system - test duration and energy - sample deflection would undoubtedly provide a great deal of valuable information on the behavior of the tested polymeric material during impact loads. The heat resistance of thermoplastic polymers is rather small, it ranges from 100 to 200°C. This disadvantage of polymers has become the reason for the intensive search for polymer materials that would be more heat resistant. Polymers reinforced with glass fiber show high heat resistance. The results of the Vicat softening temperature and heat deflection temperature (HDT) measurements are shown in Figure 6.

The presented test results (Fig. 6) show that annealing has a significant impact on the formation of thermal properties. Both the Vicat softening temperature as well as the heat deflection temperature are higher for the samples after annealing. The influence of the glass fibers strengthening the polymer matrix is also significant. It is noted that the higher the fiber content in the composite, the higher the thermal properties of the received composites. SEM micrographs of the fracture surfaces of the PP70/GF30 composites and PP50/GF50 composites are shown, respectively, in Figures 7 and 8.

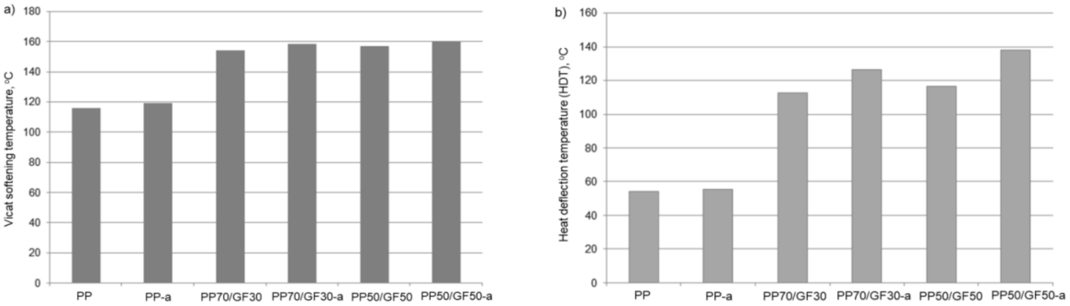

Fig. 6. Thermal properties of tested samples: a) Vicat softening temperature, b) heat deflection temperature (HDT)

Rys. 6. Właściwości cieplne badanych próbek: a) temperatura mięknienia wg Vicata, b) temperatura ugięcia pod obciążeniem (HDT)

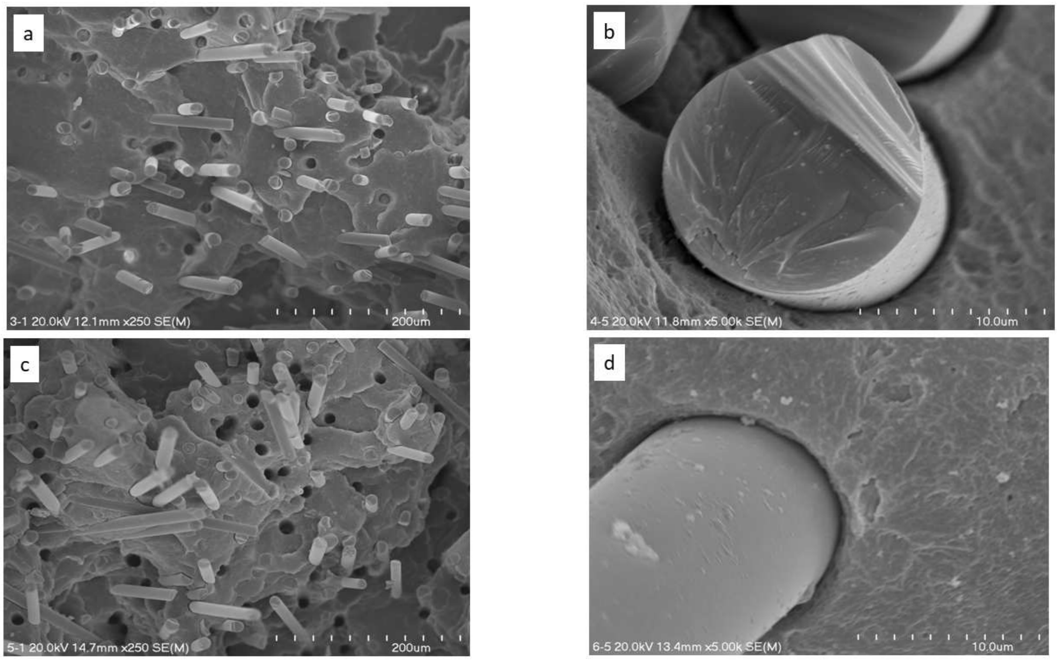

Fig. 7. Fracture microstructure: a) and b) composite PP70/GF30, c) and d) compositePP70/GF30-a (magn. 250 and 5000x)

Rys. 7. Mikrostruktura przełomu: a) i b) kompozyt: PP70/GF30, c) i d) kompozyt: PP70/GF30-a (pow. 250 i 5000x)

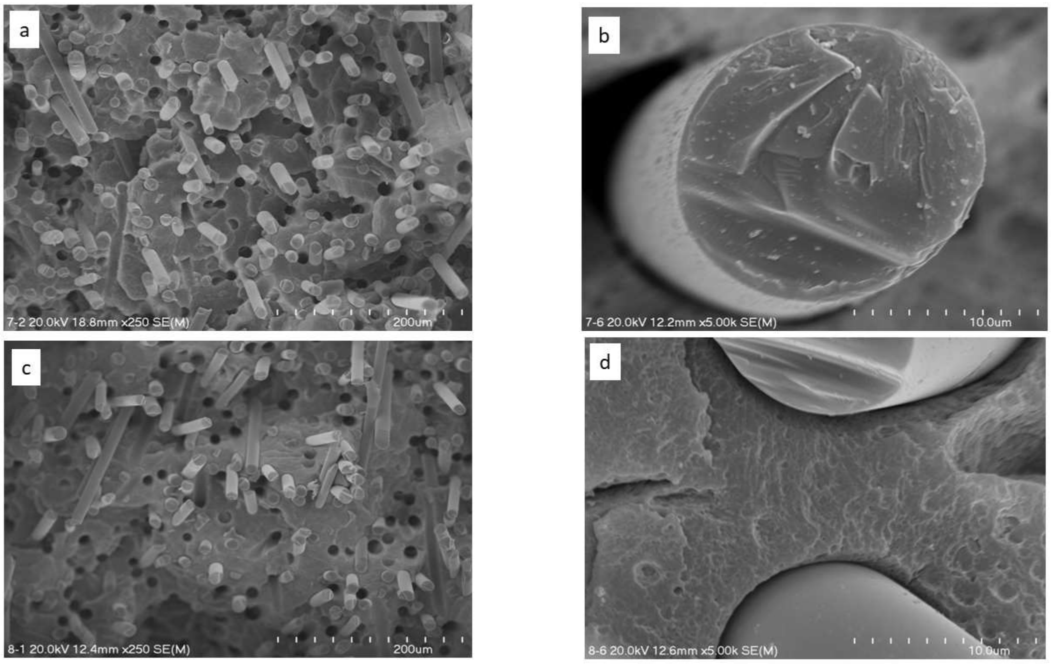

Fig. 8. Fracture microstructure: a) and b) composite PP50/GF50, c) and d) compositePP50/GF50-a (magn. 250 and 5000x)

Rys. 8. Mikrostruktura przełomu: a) i b) kompozyt: PP50/GF50, c) i d) kompozyt: PP50/GF50-a (pow. 250 i 5000x)

The SEM micrographs show the breakage of the fiber material and damage of the matrix material. During observation of the fractures, no significant fiber pullouts from the polymer matrix were noted (do not exceed 20 μm). This demonstrates the good adhesion of the glass fiber to the matrix, and thus also the correctness of the composite production technology.

SUMMARY

The glass fiber used as the reinforcing phase of polypropylene based composites is an effective way to modify the physical and mechanical properties. The use of heat treatment (annealing) causes polymorphic changes in the matrix of the composites, as well as changes in the quantitative proportion of crystalline phases. The result is advantageous composite properties. Glass fiber does not work as a factor which causes nucleation of the polypropylene crystallites, contributes to a decrease in the crystallinity of the tested composites and limits the growth of the spherulitic matrix structure. Despite this, changes in the structure of the composites caused by its presence have a positive effect on a number of mechanical parameters. In each case, annealing significantly improved the mechanical properties of polypropylenes and their composites.

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