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GLASSY CARBON FOAMS AS SKELETON REINFORCEMENT IN POLYMER COMPOSITE

Glassy carbon foams were produced by the pyrolysis process using polyurethane foam with a layer of phenol-formaldehyde resin as the precursor. The pyrolysis process was conducted in vacuum conditions at 1000°C. The pyrolysis conditions were determined on the basis of carried out thermogravimetric analysis. The basic mechanical properties like the compressive strength of the carbon foams was measured and compared with the theoretical value. Furthermore, the glassy carbon foams were applied as skeleton reinforcement in epoxy resin matrix composites. Analysis of the mechanical properties revealed that the values of hardness and compressive strength of materials with spatial carbon foam are almost two times higher than for a pure matrix applied as the reference material. The major factors that influenced the final mechanical properties are the quality of the obtained foams and the amount of carbon in the material volume. Moreover, it was proved that the application of carbon foam with low mechanical properties led to significant increases in the compressive strength of the composite materials.

Keywords: glassy carbon, foam, cellular structure, mechanical properties

PIANKI Z WĘGLA SZKLISTEGO ZASTOSOWANE JAKO WZMOCNIENIE KOMPOZYTÓW NA OSNOWIE POLIMEROWEJ

Prezentowane w niniejszej pracy pianki z węgla szklistego zostały otrzymane w procesach pirolizy preform poliuretanowych z warstwą żywicy fenolowo-formaldehydowej. Proces pirolizy został przeprowadzony w warunkach odmiennych w stosunku do stosowanych powszechnie technologiach. W tym przypadku zastosowano próżnię oraz temperaturę 1000°C. Warunki pirolizy określono na podstawie przeprowadzonej analizy termogravimetrycznej. Właściwości mechaniczne otrzymanych pianek węglowych wyznaczono na podstawie wytrzymałości na ściskanie. Otrzymane dane porównano z wartościami teoretycznymi wyznaczonymi według równania Ashby'ego i Gibsona. Ponadto, w ramach badań wytworzono kompozyty z osnową polimerową, wzmocnione prezentowanymi piankami węglowymi. Analiza właściwości mechanicznych wykazała, że wartość twardości oraz wytrzymałości na ściskanie kompozytów wzmocnionych strukturami węglowymi jest niemal dwukrotnie wyższa od wartości czystej żywicy epoksydowej - materiału referencyjnego. Określono, że najważniejszymi czynnikami mającymi wpływ na właściwości mechaniczne są jakość wytworzonej pianki oraz ilość węgla w objętości materiału kompozytowego. Ponadto zostało udowodnione, że zastosowanie pianek węglowych o niskich właściwościach mechanicznych prowadzi do znacznego wzrostu wytrzymałości na ściskanie materiałów kompozytowych na osnowie polimerowej.

Słowa kluczowe: węgiel szklisty, pianka, struktura komórkowa, właściwości mechaniczne, kompozyty z osnową polimerową

INTRODUCTION

Composite materials reinforced by carbon are efficiently used in different applications. It is caused by the excellent properties of carbon. Depending on the structure and manufacturing process, carbon can exhibit high mechanical, electrical, optical and thermal properties. The mechanical properties of composites strongly depend on the form of the reinforcement structure. The highest influence of carbon on the mechanical properties is observed in the case of fibres. The results of Kobets and Deev [1] described the specific mechanical properties of carbon fibres in detail. They presented a model where carbon fibres consist of a quasi-

-amorphous matrix and oriented carbon fibrillar. This model was confirmed by experimental data, which explained the correlation between the microstructure and high mechanical properties. These results were experimentally confirmed by many authors. Carbon fibres can be efficiently used to manufacture composites with an epoxy resin matrix [2]. It was proved that fibres made from carbon displayed higher mechanical properties than Kevlar or glass fibres. The flexural strength of laminates with carbon fibres were 2 times higher than glass fibres and almost 2.5 times higher than Kevlar fibre reinforcement [2]. In another work,

Hou et al. introduced various amounts of short carbon fibres into a metal matrix [3]. They applied the powder metallurgy process to produce magnesium matrix composites. It was observed that 1 vol.% carbon fibres led to improvement in hardness and compressive strength about 87 and 42% respectively.

Another type of carbon - carbon nanotubes (CNT) can also be used to improve the mechanical properties of polymer based [4, 5] and metal based composites [6, 7]. All the presented papers state that the most important factors are the amount and dispersion of nanotubes in the volume of the composite. M. Tarfaoui et al. revealed that a 2 vol.% amount of nanotube addition is the most favourable from the mechanical point of view [4]. However, additions of CNT lead to improvement in other properties than the mechanical one in polymer matrix composites. It can positively influence the wettability between resin and glass, and moreover, reduces composite shrinkage. On the other hand, the thermal conductivity of composites can be improved in the same way [5]. In the case of metal matrix composites, carbon nanotubes are commonly used to increase mechanical, electrical and thermal properties [6]. However, carbon nanotubes are increasingly used in new applications for materials which change tribological [7] or optical properties [8].

The most conventional form of carbon addition for different types of composites is particles, like graphite or glassy carbon particles [9-11]. 1÷5 wt.% of graphite was applied in aluminium matrix composites to improve their hardness [9]. However, due to the high tendency of reaction between aluminium and carbon, a decrease in tensile strength was observed. Moreover, amounts of graphite not higher than 3 wt.% led to increased friction properties [9].

Literature data analysis revealed the possibility to produce another type and form of carbon components. Since the 1990s, constantly growing popularity of spatial, three-dimensional structures can be observed [12, 13]. Applying this type of reinforcement gives a possibility to apply reinforcement in the whole volume of the material or only in particular places of structural elements where high stress concentration is expected [14, 15].

The presented paper is focused on an innovative form of carbon reinforcement - foams. These spatial structures exhibit more than 90% open spaced cells. This gives an opportunity to infiltrate these skeleton structures by a liquid matrix, to obtain a composite material.

EXPERIMENTAL PROCEDURE

Infiltration of PU foams by phenol-formaldehyde resin

Glassy carbon foams were manufactured based on ready-made polyurethane (PU) foams. This type of material is commonly used as filters for liquids or gases. The porosity of the PU foams is more than 90%,

while its density is in the range between 0.03 and 0.035 g·cm⁻³ (Fig. 1). PU foams may differ in size, shape and distribution of the cells. This is related to the number of cells in the length of 1 inch - pores per inch (PPI) It is possible to produce foams with a PPI between 10 and 90. The polyurethane foam exhibited a low hardness and high flexibility. This thermoplastic material is not resistant to high temperature. Due to its low temperature resistance, PU foams have to be covered by some kind of duroplastic materials. In the presented study, phenol - formaldehyde resin (FF110) was used. The PU foam was covered by a thin layer of resin obtained by the infiltration process. The thickness of the created layer has to be continuous and undamaged to ensure its protective role in high temperature conditions. On the other hand, applying too much resin leads to filling the open cells of PU foams. It causes a decreased open porosity level in the final carbon material. In the next step, the phenol resin was crosslinked using typical conditions for resin. Subsequently, the obtained foams were pyrolysed in the conditions determined by thermogravimetric measurement (Fig. 2).

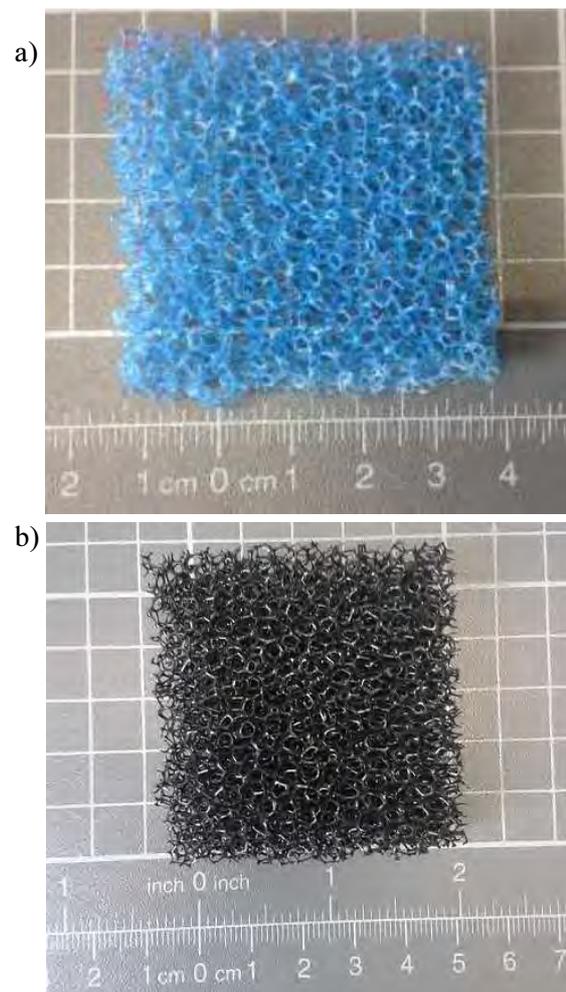


Fig. 1. Structure of polyurethane foam in initial stage (a) and after covering by layer of phenol-formaldehyde resin (b)

Rys. 1. Struktura pianki poliuretanowej w stanie wyjściowym (a) oraz po procesie pokrycia warstwą żywicy fenolowo-formaldehydowej (b)

After processing, the PU foams with the resin layer were investigated using differential thermal analysis (DTA) and thermogravimetric analysis (TG) (Fig. 2). These measurements were conducted to determine the ranges of potential reactions in the presented system. The analyses were conducted in nitrogen atmosphere. The DTA results revealed two important exothermic reactions during heating. The first of them was between 500 and 550°C, and the second between 650 and 700°C. However, a significant reduction in mass was observed in at lower temperatures (300÷550°C). The summary mass decrease of the material after processing was 40%.

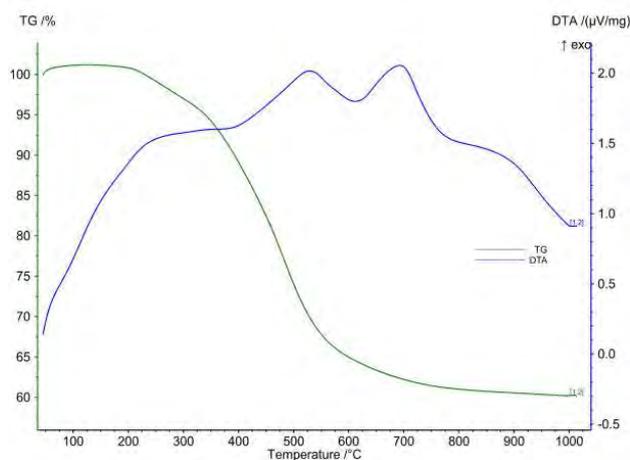


Fig. 2. Results of DTA and TG investigations for polyurethane foam covered by layer of phenol-formaldehyde resin

Rys. 2. Wyniki DTA oraz TG pianki poliuretanowej pokrytej warstwą żywicy fenolowo-formaldehydowej

Pyrolysis process

The observed results from the thermal analysis were used to describe the pyrolysis parameters. This step of technology is performed to eliminate all compounds except carbon from the analysed system. The materials in the pyrolysis process are subjected to controlled degradation processes, maintaining the amorphous structure of plastics. Finally, the pyrolysis process was conducted at 1000°C, at the heating rate of 3°C/min up to 500°C. Between 500 and 700°C, the heating rate was reduced to 2°C/min in order to ensure distribution and separation of all the compounds in the precursor material. Due to the amorphous structure of carbon, this type of material is called glassy carbon. The resultant materials consist of more than 90% carbon. The reduction in volume and mass after carbonization was lower than 40%.

Microstructures and mechanical properties of carbon foams

The microstructures of the manufactured materials were observed using a Scanning Electron Microscope, under 15 kV in the backscattered electron technique (Fig. 3). All the materials with various levels of poros-

ity 15, 30, 35 and 45 PPI after pyrolysis were characterised by an almost ideal duplication of the initial PU foam structure. All the foam cells were unfilled, and the level of porosity was on a similar level to that of PU foams. However, the final sizes were different compared to the initial foam.

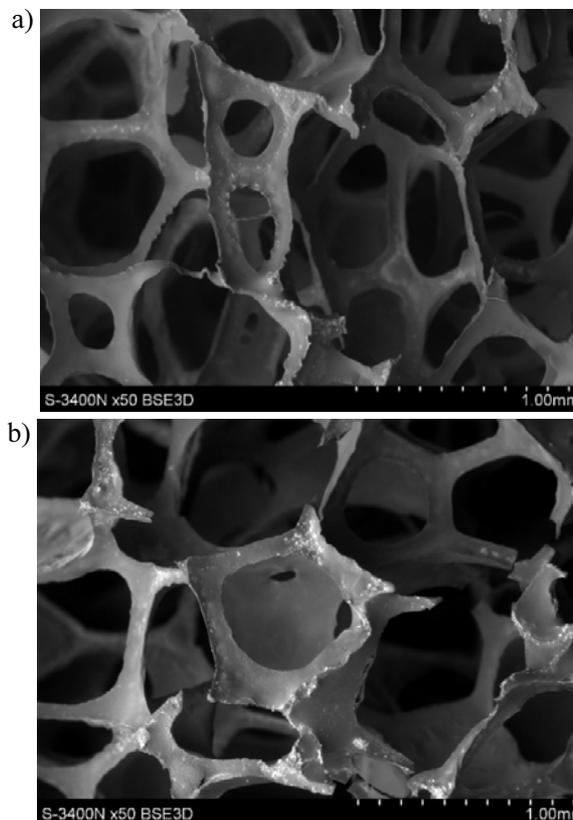


Fig. 3. Microstructure of carbon foams with 35 (a) and 45 (b) PPI after pyrolysis

Rys. 3. Mikrostruktury pianki węglowej o PPI równym 35 (a) oraz 45 (b) po procesie pirolizy

For the resultant foams made from glassy carbon, compressive strength measurements were conducted. The results are presented in Figure 4.

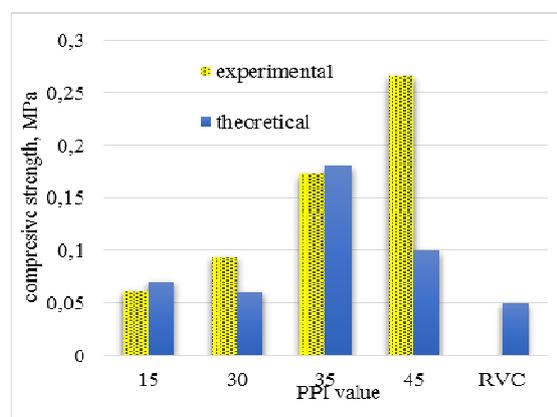


Fig. 4. Comparison of compressive strength of carbon foams obtained from Gibson and Ashby model and experimental tests [16]

Rys. 4. Porównanie wytrzymałości na ściskanie obliczonych według równania Gibsona i Ashby'ego oraz wyznaczonych w testach eksperymentalnych dla badanych pianek węglowych [16]

The analysed materials were characterised by a compressive strength value up to 0.2 MPa. For comparison, a commercial product of the Duocel company - RVC foam was tested. According to the technical information given by the Duocel company, the value of compressive strength of RVC foam should be equal to 2 MPa. However, in comparison with the foams made by the authors and the commercial product, it was proved that the mechanical properties of the authors' materials are at the same or on a higher level than the RVC foams.

The experimental data were compared with the theoretical, which were calculated based on the model presented by Gibson and Ashby [16]. In the presented model, a cubic shape with closed walls was taken into account as the basic element of the structure.

$$\sigma = C_1 \cdot \sigma_s \cdot \left(\frac{\rho_f}{\rho_s}\right)^n \quad (1)$$

where: σ - compressive strength; C_1 - value characterized by cell shape; σ_s - the strength of foam material, ρ_f - density of foam, ρ_s - density of foam material, n - exponent.

This model is a simplification of the real geometry of the foam, however, it gives an opportunity to predict selected mechanical properties like compressive strength or modulus of elasticity. During measurement, the value of C_1 was equal 0.65, exponent n was 1.5, while the value of compressive strength (50 MPa) and density ($1.4 \text{ g}\cdot\text{cm}^{-3}$) were determined based on literature data analysis and the authors' own experiments. The differences between the theoretical value and experimental data are insignificant and mainly depend on the size of the cells. In the case of low porosity, the obtained data are comparable with the experimental results. Nonetheless, more important differences are visible in foams characterised by a small size of cells and a higher number of single-wall cells. According to the established model, in compressing conditions, the foams are destroyed in the areas of bonding between cell walls (Fig. 5). The process of destruction is different from the generally adopted one for the foam destruction process. The stress-strain curve during the compression of ceramic foam revealed three important zones. Under low stress, the foam is elastically deformed. Increasing the load causes progressive, successive destruction of individual cell layers, though it is not destruction extending throughout the entire foam volume, resulting in a nearly constant stress regardless of the strain. This is related to crushing of the cell walls of single foam layers (Fig. 6). In the last zone of the stress-strain curve, a significant increase in strain can be observed. It is a result of crushing of the cell walls and areas of bonding between the cells, which caused filling of the intercellular space by already damaged parts of the cells. In the case of carbon foams, the third zone of crushing was not observed (Fig. 7).

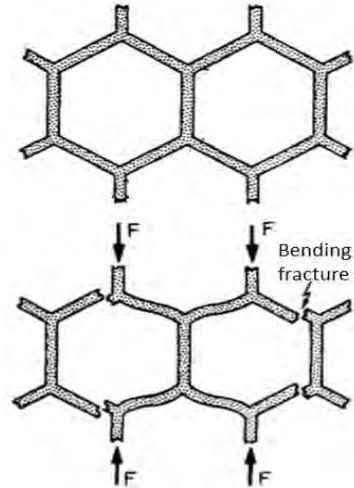


Fig. 5. Model of cellular structure destruction presented by Ashby and Mehl Medalist [17]

Rys. 5. Model zniszczenia struktury komórkowej zaprezentowany przez Ashby'ego i Medalistę [17]

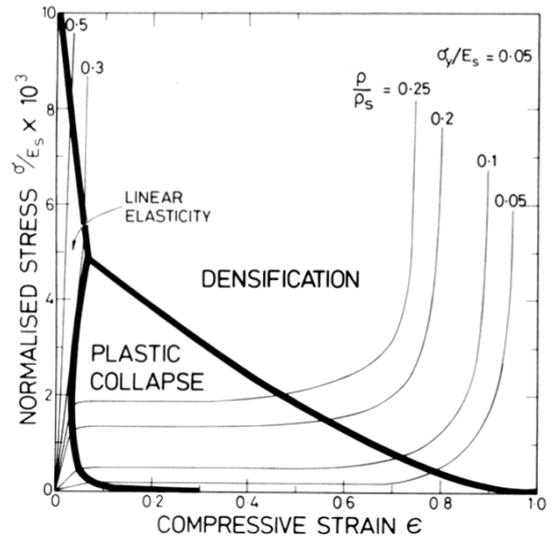


Fig. 6. Deformation mechanism map for cellular structures presented by Ashby and Mehl Medalist [17]

Rys. 6. Mapa mechanizmów deformacji struktur komórkowych zaprezentowana przez Ashby'ego i Medalistę [17]

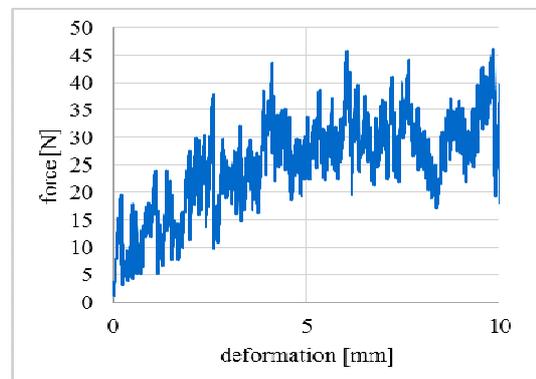


Fig. 7. Representative curve from compressive strength measurement for carbon foam

Rys. 7. Reprezentatywna krzywa wytrzymałości na ściskanie pianki węglowej

This is probably an effect of cell shape - low thickness of the cell walls in comparison with their diameter and very low number of lumps in the areas of bonding between the cells.

Composites of carbon foams with epoxy resin matrix

Subsequent foams with PPI equal to 15, 30, 35 and 45 were infiltrated by epoxy resin Duratek 1000. The infiltration process was conducted without pressure, by the gravity infiltration technique. Microstructural observations were performed using a light microscope (Fig. 8). For all the investigated materials, proper infiltration of the spatial structures was observed (Fig. 8). The obtained materials revealed a tendency of the resin to interpenetrate the carbon structure. The foams with the lowest value of PPI possessed the highest thickness of a single wall. In the case of material with a large PPI value, more homogeneous distribution of foam cells in the composite structure was observed. Small pieces of carbon foam of a cellular shape were present on the surface of the composite material (Fig. 8).

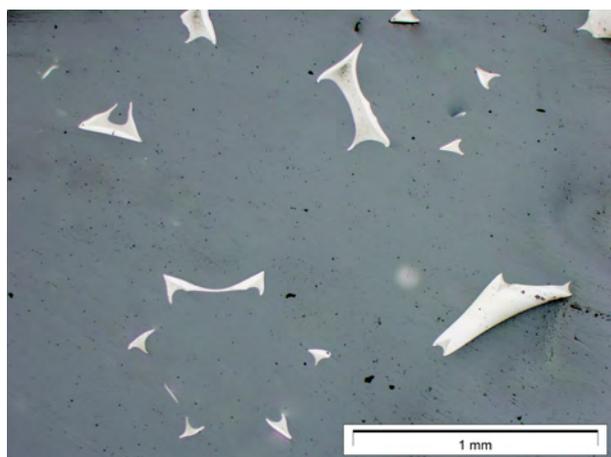


Fig. 8. Microstructure of 40 PPI foam infiltrated by epoxy resin
Rys. 8. Mikrostruktura pianki o PPI równym 40 po infiltracji żywicą epoksydową

Mechanical properties

The mechanical properties of the manufactured composites were evaluated based on hardness and compressive test data. The hardness measurement was performed by the Vickers method with a 200 g load in the space corresponding to the presence of carbon (Fig. 9a). The compressive strength tests were conducted on an INSTRON 4469 machine. Due to limitations associated with the dimensions of the initial foam precursors (PU), the samples for the strength tests were of non-standard dimensions - 20x20x40 mm. The head movement rate was 5 mm/min. It was observed that the hardness of the composites strongly depended on the PPI value (Fig. 9b). The highest hardness was noted for the material with the lowest PPI. This result is connected with the volume of the material. The single carbon wall is the thickest for the foam with the lowest

PPI value (15 PPI). If a small amount of carbon is surrounded by resin with a low hardness, the strain can be transferred to the matrix, which causes a decrease in the mechanical properties. A similar tendency was discovered in the case of the compressive strength of the composites. The compressive strength increased with a decreasing PPI value. Nonetheless, for the material with the lowest PPI, the compressive strength significantly decreased. This happened because of the defects in the carbon foam microstructure. This type of foam was characterised by some unfilled spaces in the carbon volume, which resulted in low resistance in compressive conditions. However, it has to be noted that it is possible to obtain a high compressive strength of the composite material, using a spatial structure with low mechanical properties.

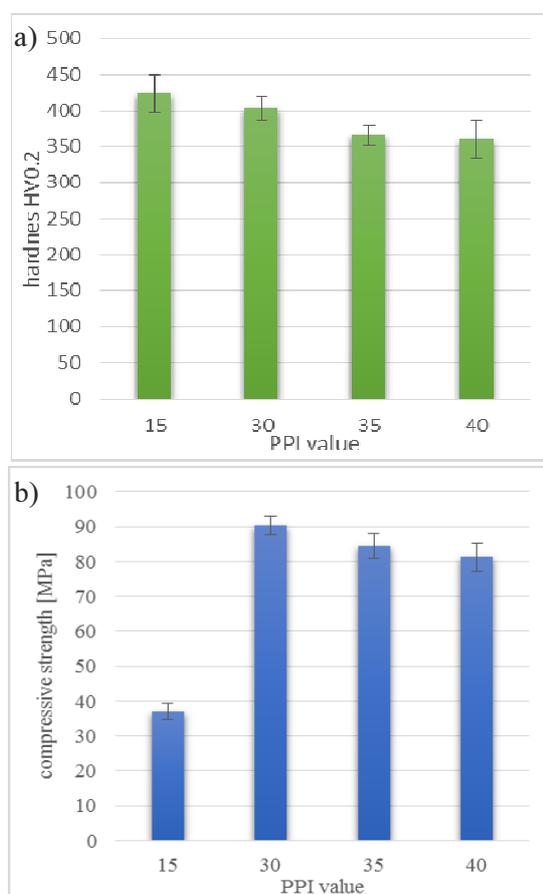


Fig. 9. Influence of PPI value on hardness (a) and compressive strength (b) of polymer matrix composites reinforced by carbon foams

Rys. 9. Wpływ ilości porów na całkowitą twardość (a) oraz wytrzymałość na ściskanie (b) materiałów kompozytowych wzmocnionych piankami węglowymi

CONCLUSIONS

The presented research confirmed that the obtained carbon foam can be applied as a reinforcement of composite material. The spatial structures of foam with a high level of open porosity give an opportunity for infiltration by a liquid matrix, e.g. polymers or metal matrix. By using various kinds of PU foam (different

PPI), the amount of reinforcing agent in the matrix value can be controlled. Notwithstanding, the most beneficial effects were noted during compressive strength measurements. It was proved that it is possible to obtain high mechanical properties of the composite material by applying a carbon cellular foam characterised by low compressive strength. Moreover, application of this type of reinforcement limits problems with composite materials that are typical for classic methods, like casting. The obtained structure of the material is similar to matrix and reinforcement channels which are interpenetrated by each other. This kind of structure exhibited high homogeneity, without problems of segregation, sedimentation or clusters. This form of carbon reinforcement can be used in a variety of composite groups, not just with a polymer matrix, but also in metal or ceramic matrix composites. Furthermore, using this type of material in the form of a precursor gives an opportunity to apply reinforcement only in required places, which is profitable from the economic and environmental point of view.

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