PhD thesis

by

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The effect of addition of glassy carbon particles at different grain size on properties of heterophase HDPE matrix composites made by FDM 3D-printing

Wpływ wielkości ziarna węgla szklistego na właściwości heterofazowych kompozytów HDPE wytworzonych metodą druku 3D FDM.

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Glassy carbon (GC) is a material with a unique combination of properties. It has high hardness and chemical resistance like ceramic materials, while maintaining high thermal and electrical conductivity like typical carbon materials. Thanks to this, it is a material with great potential and now it is successfully used in electrochemistry for electrodes. In addition, its biomedical potential is being developed thanks to its biocompatibility. However, this material also has potential as reinforcement in composite materials. In recent years, scientific works have appeared on glassy carbon as reinforcement of materials based on metals, i.e., aluminium, magnesium, and copper. These works show that glassy carbon allows to obtain materials with good sliding properties while maintaining good strength. In addition, a works demonstrating the potential of glassy carbon in composites based on resins and thermoplastics can be found. In both cases, glassy carbon allows to improve tribological properties, while in the case of thermoplastics there are works showing an improvement in electrical properties. However, the potential of glassy carbon as a reinforcement for thermoplastics is still not sufficiently understood.

The aim of the study was to investigate the influence of glassy carbon on the properties of composites based on a thermoplastic material. For this purpose, high-density polyethylene (HDPE) was chosen as the matrix, which can be used as a material for tribological and microelectronics applications. The research focuses in particular on the influence of grain size on the properties of the HDPE matrix. The effect of glassy carbon on the properties of heterophase composites exhibiting desirable tribological and piezoelectric properties was also investigated. An additional aspect of the work was the study of materials made using the 3D printing method (Fused Deposition Modeling – FDM), due to the growing interest of the composite industry in HDPE filaments. Because of the above assumptions, the thesis was formulated that it is possible to make HDPE/GC composite filaments for FDM 3D printing and obtain prints with special tribological and piezoelectric properties. In the work as a reinforcement of composites for tribological applications, nano Al_2O_3 was chosen due to the widely researched potential of use as a biomedical material for the hip joint. For piezoelectric composites, antimony sulfoiodide (SbSI) was chosen as the reinforcement due to its documented good connections with the polymer matrix.

The research part included three main elements: development of a procedure glassy carbon with two different grain sizes preparation, testing the impact of glassy carbon on the polymer matrix and investigate the properties of tribological and piezoelectric composites with the addition of glassy carbon. In the first part, by using high-energy milling, a glassy carbon powder with an average grain size $D_{4/3}$ = 5.17 µm was obtained, which was classified as micrometric (µGC) and glassy carbon powder with an average grain size $D_{4/3}$ = 0.58 µm, which was classified as submicrometric (sµGC). Next, the influence of both fractions on the crystallization process and the grain size of the HDPE matrix was investigated. Using differential scanning calorimetry (DSC), glassy carbon was found to affect the crystallization process of polyethylene, and sµGC significantly interferes with this process, constituting an obstacle for polymer chains. Based on X-ray analysis of the structure, it was found that glassy carbon is a heterogeneous nucleus of the crystallization process of the tetragonal phase of polyethylene and leads to a reduction in the grain size of the polymer matrix. Mechanical tests have shown a significant increase in tensile strength for both types of reinforcement. Electrical studies were also carried out, which showed that glassy carbon improves the electrical conductivity of polyethylene and percolation threshold of 5% by volume for μGC and 4% for sμGC were achieved.

In the case of research on heterophase composites, samples were prepared by 3D printing. In the case of composites containing nano-Al2O3, tribological studies were carried out. It has been shown that the addition of glassy carbon allows the formation of carbon tribofilm allowing for self-lubrication during friction. Additionally, GC decreased wear rate in the case of composites containing nano-Al2O3. No significant effect of grain size on the behaviour of tribological composites was found. Studies on piezoelectric composites containing SbSI have shown that the addition of glassy carbon significantly increases the voltage signal and the power generated. The largest increase was shown for a composite containing sμGC as reinforcement and is due to a significant improvement in the electrical conductivity of the polymer matrix.