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COMPOSITES THEORY AND PRACTICE

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PHYSICAL PROPERTIES OF POLYOXYMETHYLENE COMPOSITE WITH QUARTZ SAND AFTER UV AGEING

The results of examinations of polyoxymethylene (Tarnoform) with quartz sand composites are presented. Investigations were made for composites with quartz sand covered with a 20% type A 1100 aminosilane water solution. A composite with a 30% filler content was made using an extrusion machine collaborating with a granulator. Composites of lower filler contents (10 and 20%) were made by the addition of a proper amount of Tarnoform to the 30% composite. The samples for the examinations were made using a KraussMaffei KM65-160C1 screw injection moulding machine. Investigations were conducted on the samples before as well as after UV ageing. Investigation of the mechanical properties: tensile strength and hardness were made, and also the thermal properties, gloss and color were determined. The aim of the investigations is to determine the influence of the filler and UV ageing on the composite properties and to receive a new, cheaper constructional material. The lowest value of melting enthalpy of the POM/ quartz sand composite was obtained from samples after UV ageing. An increase in the lightness value after the ageing process of POM filled with quartz sand was obtained. The character of the changes of the a* and b* coordinate values for the examined materials before and after the ageing process was evaluated, which proves the essential influence of the filler addition on the colour change. The tensile strength of the composite decreases, while the hardness increases as the content of quartz sand increases both before and after the ageing process.

Keywords: **composites, thermal properties, tensile strength, color, gloss, polyoxymethylene, quartz sand**

WŁAŚCIWOŚCI FIZYCZNE KOMPOZYTU POLIOKSYMETYLENU Z PIASKIEM KWARCOWYM PO PROCESIE STARZENIA PROMIENIAMI UV

Proces starzenia kompozytów polimerowych pociąga za sobą zmianę właściwości użytkowych tych materiałów. Przewidywanie zmian właściwości na skutek procesu starzenia odgrywa dużą rolę w planowaniu składu, jak również w sporządzaniu kompozytów. W pracy przedstawiono wyniki badań zmiany właściwości termicznych, mechanicznych, barwy i połysku po procesie przyspieszonego starzenia promieniami UV kompozytu polioksymetylenu z piaskiem kwarcowym. Badania właściwości termicznych przeprowadzono metodą DSC. Zmiany barwy określono metodą CIELab, a połysku w zakresie kąta odbicia 20 i 60°. Badania przeprowadzono na próbkach wytworzonych metodą wtryskiwania. Zarejestrowano wpływ procesu starzenia na wartość entalpii topnienia zarówno polioksymetylenu, jak i kompozytów z piaskiem kwarcowym oraz zmiany zakresu temperatury topnienia fazy krystalicznej. W pomiarach barwy uzyskano zmiany jasności badanych próbek. Określono charakter zmian wartości współrzędnych a* i b* badanych materiałów, który wskazuje na wpływ starzenia promieniami UV oraz napełniacza na zmianę barwy. Zarejestrowano wzrost wartości jasności oraz zmniejszenie połysku badanych kompozytów po procesie starzenia. W miarę zwiększania zawartości napełniacza zmniejsza się wytrzymałość na rozciąganie kompozytu, zwiększa twardość zarówno dla kompozytów przed, jak i po procesie starzenia.

Słowa kluczowe: **kompozyty, właściwości termiczne, wytrzymałość na rozciąganie, barwa, połysk, polioksymetylen, piasek kwarcowy**

INTRODUCTION

The modification of polymers' properties widens their application range. One of the modification methods consists in polymer filling with proper fillers e.g. fly ashes, graphite, carbon black, glass fibre, molibdene disulphide, metal filings and powders. Polymer composites belong to widely used constructional materials. When using polymer composites as constructional materials, their chemical constitution, physical and usable properties as well as processing technology and application possibilities should be known [1-6]. There is a need to carry out further investigations on the properties of these materials and also on the methods of constituting their physical and usable properties. Actions taken towards receiving polymer composites with specific properties are more economically effective than searching for new materials. This way of obtaining specific materials by physical modification is carried out in highly industrialised countries, and in many papers, it is included among of the future methods of obtaining new generation constructional materials. Therefore, it is important to find such fillers which do not require excessive preliminary preparation - surface preparation, the removal of active compounds before their addition to the composite, and filler introduction into the composite should be possible at low costs and not require complicated operations. Filler addition should also enable one to control the composite properties in an exactly determined way [7-10].

The paper attempts to clarify the effect of the filler in the form of quartz sand on the POM properties. Quartz sand is a cheap and readily available mineral material.

This work was carried out to investigate the influence of filler contents on the properties of polyoxymethylene/quartz sand composites such as: thermal properties, tensile strength, hardness, color and gloss. The influence of ultraviolet radiation ageing on these properties was also investigated. Prediction of the properties and length of use plays an important role in the planning of the composition as well as in the manufacture of polymer products. Resistance to the effects of photochemical degradation occurring under the influence of UV radiation is very important [11].

MATERIALS AND INVESTIGATION METHODOLOGY

The Polish-made thermoplastic Tarnoform, produced by Zakłady Azotowe S.A. in Tarnów was used in the experiments. It is a sort of polyoxymethylene, which has higher strength parameters and is used for the production of technological elements by the injection moulding method. Quartz sand from the Polish mine "GRUDZEN LAS" was used for making the composites. Information about the physical properties and chemical constitution of the used quartz sand are given in Table 1. The samples were made with quartz sand covered with a 20% aminosilane type A 1100 water solution, which is a bonding agent and it causes an increase in adhesion. A composite with 30%, by weight, quartz sand content was made by extrusion moulding of a dried Tarnoform/quartz sand compound and granulation of the extruded composite. A single-screw extruding press with a straight extrusion head, equipped with a compound dosage system and a degassing system, was used to make the composite extrusion moulding. Other composites of 10 and 20% filler contents were made by blending of the 30% composite with an unfilled plastic, in a proper ratio. The samples for the examinations were made by injection moulding, using a KraussMaffei KM65-160C1 screw injection moulding machine. Samples from Tarnoform were also made to compare the properties of the composites and unfilled polymer. Optimal properties of the injected samples were obtained under the following processing conditions: pressure limit in the plasticizing unit: 120 MPa, holding pressure: 70 MPa, holding time: 25 s, cooling time: 10 s, melt temperature: 200°C, mould temperature: 80°C.

TABLE 1. **Physical properties and chemical constitution of quartz sand**

TABELA 1. **Właściwości fizyczne i skład chemiczny piasku kwarcowego**

main fraction	0.10/0.16/0.071		
homogeneity index	91%		
average grain size	0.14 mm		
sintering temperature	1550°C		
chemical constitution [%]	SiO_2	Fe_2O_3	carbonaceous
	99.20	0.10	0.08

The polyoxymethylene composite before injection molding was dried in a "SHINI" heating cabinet at 90°C for 3 h. The ageing process was performed in a test chamber using a UV high-pressure mercury discharge lamp. The time of the ageing process in the chamber was calculated from the data, assuming from the literature [12, 13] 1000 kWh/m^2, the total radiation power per year was found to be 9.26 days, which the lamp discharges using a certain power, corresponding to four years of solar radiation.

Tests of the thermal properties were carried out by means of a scanning microcalorimeter PC 200, manufactured by Netzsch. DSC curves were acquired while heating the samples at the heating rate of 10°C/min, within the temperature range from 50 up to 230°C. In order to minimize the skin-core effect, the samples were cut parallel to the molten polymer flow direction in the injection mold cavity. The software of the DSC apparatus was used to calculate the melting enthalpy. The software allows investigation of the melting process of the sample in the considered temperature range and calculation of the area between the thermographic curve and the base line in the endothermic peak temperature range. The mass of the samples was in the range of 8 to 12 mg. The samples were weighed using scales produced by SARTORIUS, with the accuracy of 0.01 mg, self-calibration and a closed measurement chamber.

The study of the color was performed by means of the CIELab method using a SP60 colorimeter, manufactured by X-Rite. The results are presented in the form of chromaticity coordinates L*, a*, b*.

The lightness of a sample is represented by the symbol L* and this value is based on the percent of light reflectance. If the L* value is zero, the sample is black. If the value is 100, the sample is white. Any sample that is void of hue and falls somewhere between 0÷100% reflectance will be a variation of gray. The a* and b* coordinates have no specific numerical limits. Positive a* is red. Negative a* is green. Positive b* is yellow. Negative b* is blue.

The gloss was determined using an Elcometer 406L Statistical Gloss Meter. The Gloss Meter comprises a light source which is directed at the test surface at a specified incidence angle and a receptor which is located at the mirror reflection of the incident beam. The gloss change was determined by the reflection angles of 20 and 60°.

The tensile strength and elongation at break were determined using the testing machine ”Hegewald & Peschke” type Inspekt Desk. The results of the hardness tests were obtained with a ball indentation tester.

The investigations were conducted according to conventional standards (ISO).

RESULTS OF INVESTIGATION AND DISCUSSION

The properties of the composite were determined from the samples in the form of injection moulds. As a result of such a method of sample preparation, the properties were conditioned by the processing parameters. The investigations were performed in order to estimate the processing capability and usability of POM composites with quartz sand addition.

The results of differential scanning calorimetry investigations of the polyoxymethylene with quartz sand composite before and after the ageing process were presented in the form of thermographic curves (Fig. 1). The values calculated on the basis of DSC thermographic curves are listed in Table 2.

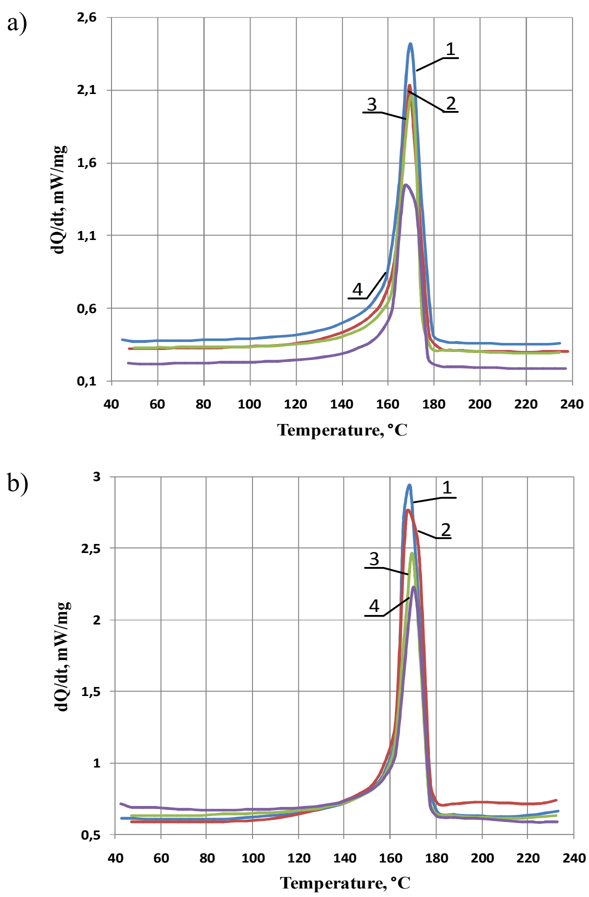

Fig. 1. Thermograms DSC of quartz sand composites: a) before ageing, b) after ageing; 1, 2, 3, 4 - tested material

Rys. 1. Termogramy DSC kompozytów z piaskiem kwarcowym: a) przed starzeniem, b) po starzeniu; 1, 2, 3, 4 - badany materiał

As a result of the UV ageing of polyoxymethylene, the melting enthalpy of polyoxymethylene decreased. The reason for such a change in the values is the decrease in molecular weight caused by macromolecules cracking. The degree of chain branching and molecular weight distribution significantly influence the crystallinity of polyoxymethylene that is a significant factor which impacts the performance properties of this material. The DSC investigations prove the decrease in the melting enthalpy of the POM/quartz sand composites after the ageing process. For the composite samples, the temperature of the highest melting rate was not reduced but the range of melting temperature was changed significantly. However, the shape of the thermograms is insignificantly changed.

TABLE 2. **Results of DSC investigations of polyoxymethylene with quartz sand composites obtained from calculations by Netzch programme**

TABELA 2. **Wyniki badań metodą DSC kompozytów polioksymetylenu z piaskiem kwarcowym uzyskane z obliczeń programu Netzch**

Before UV ageing				
Material		Enthalpy [J/g]	Melt temperature range [ºC]	Melt temperature – peak maximum [ºC]
1	POM	151.4	162.6÷176.7	169.6
2	POM +10% quartz sand	153.6	162.6÷175.4	169.7
3	POM +20% quartz sand	164.7	162.9÷173.9	170.5
4	POM +30% quartz sand	147.4	163.8÷173.8	170.1
After UV ageing				
1	POM	137.9	162.3÷175.8	169.2
2	POM +10% quartz sand	147.4	162.4÷174.7	167.8
3	POM +20% quartz sand	136.7	162.7÷172.1	170.1
4	POM +30% quartz sand	135.5	163.0÷171.5	169.1

The results of the gloss tests of the composite samples are shown in Figure 2.

Lower gloss values were recorded for the composite samples after UV ageing, and both the reflection angles of 20° and 60° recorded a similar trend of change. Higher gloss values were recorded for the polyoxymethylene samples.

Figure 3 summarizes the recorded a*, b* and L* coordinate values of the test composite before and after UV ageing. The samples of the composite were characterized by a greater b* coordinate value and slightly greater a* coordinate value. This increased the saturation of the green - yellow shade of the polyoxymethylene with quartz sand composites. Ageing causes an increase in the composite polyoxymethylene with quartz sand L* value, which means that the sample has become clearer. The character of the changes in the a* and b* coordinate values of the composite demonstrates the effect of UV ageing to change the color. Samples of the composite after ageing are characterized by smaller a* and b* coordinate values. UV ageing of composite polyoxymethylene with quartz sand increased the saturation of the blue - green shade.

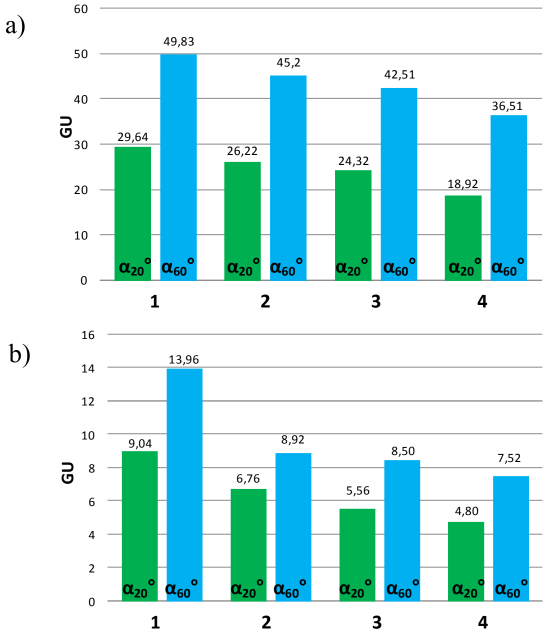

Fig. 2. Gloss of examined composites: a) before ageing, b) after ageing; 1, 2, 3, 4 - tested material

Rys. 2. Połysk badanych kompozytów: a) przed starzeniem, b) po starzeniu; 1, 2, 3, 4 - badany materiał

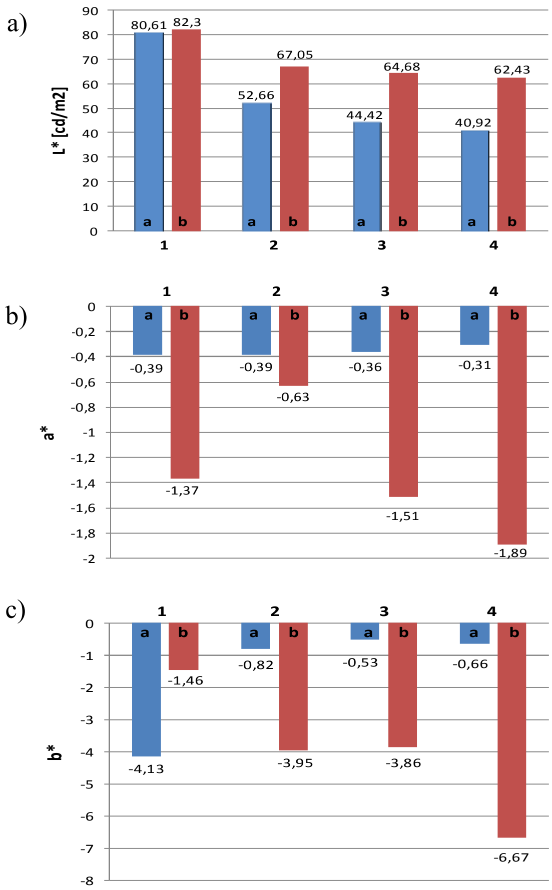

Fig. 3. a) Lightness L* of examined polymer materials, b) value of a* coordinate for examined polymer materials, c) value of b* coordinate for the examined polymer materials; a - before ageing, b - after ageing; 1, 2, 3, 4 - tested material

Rys. 3. a) Jasność L* badanych materiałów polimerowych, b) współrzędna a* badanych materiałów polimerowych, c) współrzędna b* badanych materiałów polimerowych; a - przed starzeniem, b - po starzeniu; 1, 2, 3, 4 - badany materiał

On the grounds of the presented investigation results, it can be stated that the filler has a significant effect on the mechanical properties of the composites, and their values depend on the filler percentage and UV ageing process. The diagrams from the tension test are presented in Figure 4. The results of the hardness tests of the composite samples are shown in Figure 5. It was found that the tensile strength of a composite decreases together with the filler percentage. For the 30% filler content, it was found that the tensile strength decreased by 31% in comparison to the results received for polyoxymethylene. For the samples after ageing, one can observe a decrease in the tensile strength of the tested material as opposed to the samples before ageing. For polyoxymethylene, it was found that the tensile strength decreased by 68% compared to the results received for polyoxymethylene before ageing. During the investigation of the composites after UV ageing, an increase in tensile strength was observed. For the 20% filler content, it was found that the tensile strength increased by 52% in comparison to the results received for polyoxymethylene after ageing.

According to the presented investigations, one can conclude that along with an increase in filler participation in the composite, hardness rises. As a result of UV ageing of polyoxymethylene and polyoxymethylene with the filler addition, the hardness values decreased. Higher values of hardness were recorded during the testing of the polyoxymethylene with filler. On the grounds of the presented results of the investigations, it can be stated that the composite with the 30% quartz sand content has the highest hardness.

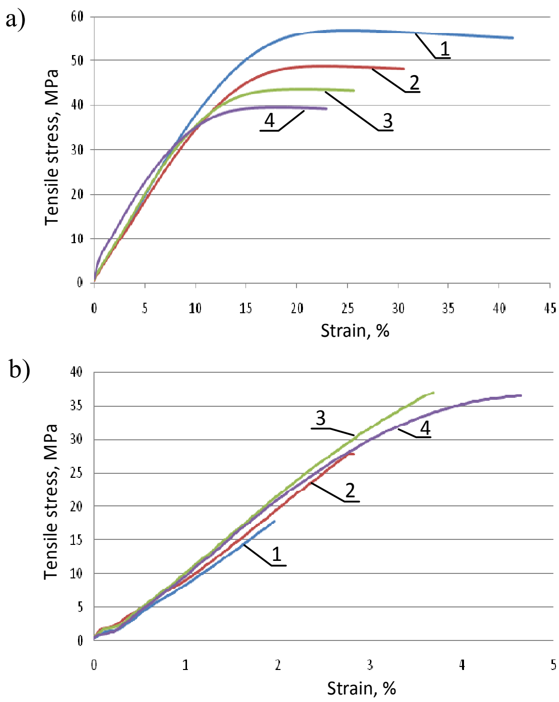

Fig. 4. Relationship between stress σ and strain: a) before ageing, b) after ageing; 1, 2, 3, 4 - tested material

Rys. 4. Zależność naprężenia σ od odkształcenia: a) przed starzeniem, b) po starzeniu; 1, 2, 3, 4 - badany materiał

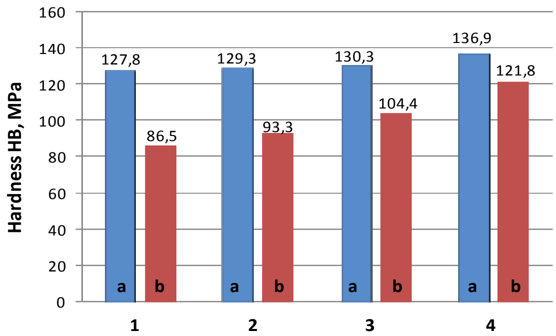

Fig. 5. Influence of filler content, and ageing on hardness of polyoxymethylene and its composites with quartz sand: a - before ageing, b - after ageing; 1, 2, 3, 4 - tested material

Rys. 5. Wpływ zawartości napełniacza i starzenia na twardość polioksymetylenu i jego kompozytów z piaskiem kwarcowym: a - przed starzeniem, b - po starzeniu; 1, 2, 3, 4 - badany materiał

CONCLUSIONS

The properties of polymeric material depend on the presence of filler. The analysis of DSC studies show a significant effect of the UV ageing process and filler content on the thermal properties of the composite polyoxymethylene with quartz sand. Based on DSC thermograms, changes in the melting range of the crystalline phase and the beginning of the crystallization temperature of the samples before and after UV ageing were revealed. No significant change in temperature was registered at which crystallization occurs at maximum speed. The DSC results show a decrease in the melting enthalpy of the composite samples after UV ageing, which influences the change of the performance of the material. In the study of the color and gloss of the composite polyoxymethylene with quartz sand, it was observed that they change, depending on the ageing process. The samples of the material after the ageing process were characterized by a greater gloss and a different color. The change in the value of coordinates a*, b*, and lightness L*, the gloss value, and mechanical properties can be explained by the different structure of the composite before and after ultraviolet radiation ageing (crystallinity, amorphous). On the grounds of the presented investigation results, it can be stated that after the ageing process the composite has better mechanical properties (tensile strength, hardness) compared to polyoxymethylene after ageing.

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