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THE MECHANICAL CHARACTERIZATION OF COMPOSITES
BASED ON POLYOXYMETHYLENE AND THE EFFECT OF SILICONE ADDITION
ON THE MECHANICAL BEHAVIOUR OF MANUFACTURED COMPOSITES

CHARAKTERYSTYKA MECHANICZNA KOMPOZYTÓW
NA BAZIE POLIOKSYMETYLENU I WPLYW DODATKU SILIKONU
NA ZACHOWANIE MECHANICZNE WYTWORZONYCH KOMPOZYTÓW

Abstract

The mechanical properties of manufactured composites based on polyoxymethylene (Tarnoform 300) were determined. POM composites reinforced with ultra-high molecular weight silicon, thermoplastic polyurethane, and special chalk in order to reduce abrasiveness and aramid fibres were manufactured. The basic mechanical properties (tensile strength (σ_M), modulus of elasticity (E_t), strain at break (ϵ_B), flexural modulus (E_f) and flexural stress at 3.5% strain (σ_s)) were evaluated at three temperatures -20, 20 and 80°C. The density and Charpy impact of the produced composites were examined. In order to make reference to the effects of reinforcement and determine the characteristics of their microstructure SEM, images were taken.

Keywords: polyformaldehyde, additives, modification of structure, properties

Streszczenie

Określono właściwości mechanicznych kompozytów na podstawie polioksymetyleny Tarnoform 300. Wytworzono kompozyty wzmocnione silikonem o ultrawysokiej masie cząsteczkowej, termoplastycznym poliuretanem, kredą obniżającą ścieralność oraz włóknem aramidowym. Wyznaczono podstawowe właściwości mechaniczne (wytrzymałość na rozciąganie (σ_M), moduł sprężystości przy rozciąganiu (E_t), odkształcenie przy zerwaniu (ϵ_B), moduł sprężystości przy zginaniu (E_f) oraz naprężenie przy odkształceniu 3,5% (σ_s)) w trzech temperaturach -20, 20 and 80°C. Określono gęstość oraz udarność wg Charpy'ego dla wytworzonych kompozytów. W celu oceny efektów wzmocnienia i cech mikrostruktury wykonano mikrofotografie SEM.

Słowa kluczowe: poliformaldehyd, dodatki, modyfikacja struktury, właściwości

1. Introduction

Polyoxymethylene (POM) is a semicrystalline polymeric material. It is an engineering thermoplastic. POM is characterized by low friction and wear rate. It has an excellent balance of mechanical properties and it is chemically resistant to most solvents, chemicals and fuels at room temperature. Hence, such polymers are used to serve as an alternative to metals. Among the polymers obtained from the polymerization of aldehydes, POM is the only one that could reach commercial significance [1]. Additives on polyoxymethylene are used in order to easy processing (lubricating agents, processing aids, nucleating agents), performances (fillers, impact modifiers), lifetime increase (antioxidants, compounds reacting with secondary reaction products, UV stabilizers and flame retardants) and aspect properties (pigments). POM compounding can be relatively complex and additives are scarcely used alone, they react with each other and influence the properties [1]. Polymer composites based on POM matrices have been widely examined due to the fact that conventional materials no longer meet the needs and expectations of modern engineering. Chenghe Liu et al. [2] reported that using short basalt fibre as reinforcement POM enhances its mechanical properties. It was found that the 20wt.% fibre content increased the mechanical properties. The tensile strength was higher by 27.45%, impact strength increased by 9.65% and flexural strength by 18.11% with compared to pure POM. But its tribological properties were worse with the addition of the basalt fibres. Yatao Wang et al. [3] also studied composites based on POM but reinforced with long basalt fibre. The results obtained were similar. The addition of BF built up mechanical properties and impact strength, but tribological properties such as friction coefficient and wear rate dropped. However, thermal stability increased compared to unmodified POM. Wei Luo *et al.* [4] investigated the effect of morphology of aramid fibres and particles on the friction and wear of polyoxymethylene (POM)/ aramid composites under dry friction conditions. The results showed that the addition of short aramid fibres (ASF) and particles (AP) affected the friction and wear of POM composites with aramid in two different ways due to the presence of reinforcement in the composites. Mariola Wojciechowska et al. [5] examined the influence of different amounts of glass fibre (10-30wt.%) on the mechanical properties of POM composites. For composition with 30wt.% content of glass fibres the ultimate tensile strength exhibited elevation by 96% but also deterioration in elongation after break. The impact strength and hardness also increased nearly 100% and 40%, respectively. The mechanical and tribological properties of the polyoxymethylene (POM) composite reinforced with carbon fibre (5-25vol%) were investigated. The tensile strength and modulus rose with increasing volume fraction. It was also observed that the friction coefficient for carbon fibre reinforced POM was lower than pure POM [6]. Natural fibres are also widely used as reinforcement of POM composites [7-10], for example the mechanical and physical characteristic of composites composed of polyacetal and cellulose were investigated in [11-13] the POM/CeF composites possessed high modulus, stiffness and had low wear rate. The results of SEM observation indicated good interfacial adhesion between the monofilaments of the CeF and the POM matrices during the fracture process. Afsaneh Fakhar et al. [14] investigated the tribological properties of polyoxymethylene (POM) composites with aramid fibres (20wt.%) and PTFE (13wt.%). The results showed that both of additives reduced the

coefficient of friction and abrasive wear of the material but also reduced the breaking energy which eliminated the role of abrasive wear in the conditions. The influence of adding copper and PTFE particles on thermal conductivity and tribological properties of POM composites was determined by Junqing He et al. [15–16]. The results showed that the addition of 3% by weight of Cu to polyoxymethylene had little effect on thermal conductivity and slightly decreased the coefficient of friction and abrasion rate, while the PTFE addition significantly reduced both friction coefficient and material wear. Composites are present in a wide variety of industries and technologies, but this does not slow down the work rate on new materials. The aim of this study is investigation of the effect of silicon addition, aramid fibre and thermoplastic polyurethane on mechanical properties of POM composites as a first stage of investigation of the tribo-mechanical behaviour of manufactured composites.

2. Experimental part

2.1. Materials and methods

The standard dumbbell samples and bars were made at the Plastics Laboratory of Azoty Group SA in Tarnow using the Engel ES 200/40 HSL injection moulding machine at temperatures indicated by the manufacturer for Tarnoform T-300. The granules of the composition were prepared by twin-screw extrusion with cold granulation using a line of compounding. The selected and manufactured materials which were used for the study are presented in Table 1.

Table 1. Description of manufactured and examined materials

Index	Additives	Description
POMSM	95wt.% Tarnoform 300 (POM) + 5wt.% Dow Corning MB40-006 Masterbatch-	polyoxymethylene (POM) with an ultra-high molecular weight silicone additive
POMSO	100wt.% Tarnoform 300 SO NAT	ready mix in the form of POM granules with silicone for injection to reduce friction coefficient and abrasion in plastic-plastic systems
POMAR	80wt.% Tarnoform 300 + 10wt% Aramid fiber	ready mix polyoxymethylene with aramid fibre to improve abrasion resistance and reduce coefficient of friction
POM2U	80.wt% Tarnoform 300 (POM) + 20wt.% TPU	polyoxymethylene (POM) with the addition of thermoplastic polyurethane to improve the damping of mechanical vibrations and noise reduction
POMBK5M	95wt.% Tarnoform 300 BK + 5wt.% Dow Corning MB40-006 Masterbatch	polyoxymethylene with addition of special chalk and silicone lubricant to reduce abrasion

2.2. Method of testing

The basic physical and mechanical tests of polyacetal composites were accomplished. Density was estimated by the hydrostatic method using a RADWAG WAS 22W scale. The mechanical properties were tested by a static tensile test (PN-EN ISO 527-1:20100) and the three point flexural tests according to the PN-EN ISO 178:2011 standard. Measurements were obtained using an MTS Criterion Model 45 universal testing machine, with a measuring range up to 30 kN using the MTS axial extensometer. The test speed was set up to 10mm/min. The mechanical properties, such as tensile modulus, tensile strength, strain at break as well as flexural modulus and flexural strength were determined. A Charpy impact test (PN-EN ISO 179-1:2010) was examined on unnotched specimens using a Zwick HIT 5.SP. The microstructure observations were made on the gold-sputtered tensile-test fracture surfaces of specimens with the use of a Scanning Electron Microscope JEOL JSN5510LV. The values were obtained from an average at least of 5 specimens.

3. Results and discussion

The mechanical properties are affected by many factors, such as: temperature, time and speed of deformation, duration of the test, and geometry of the samples. The obtained results are presented in Figures 1–2. The determined parameters are summarized in Table 2.

Table 2. Mechanical properties of the tested materials

Sample	Density [g/cm ³]	Tensile strength [MPa]	Tensile modulus [MPa]	Strain at break [%]	Flexural strength at 3,5% of stain [MPa]	Flexural modulus [MPa]	Impact Strength [kJ/m ²]
POMT300*	1.410	62	2800	50	61	2500	200
POM5M	1.401	54.0 ± 0.5	2966 ± 102	37 ± 11.5	80.9 ± 1.8	2719 ± 37	96.5 ± 14.7
POMSO	1.400	51.3 ± 0.7	2894 ± 82	37.8 ± 3.8	77.9 ± 0.4	2645 ± 5	176.1 ± 11.4
POMAR	1.413	70.4 ± 0.2	3821 ± 458	5.5 ± 0.2	92.1 ± 3.4	3286 ± 264	51.5 ± 5.4
POM2U	1.360	41.3 ± 8	1841 ± 306	63.0	50.4 ± 0.8	1713 ± 52	not break
POMBK5M	1.426	51.3 ± 0.8	3105 ± 118	41.5 ± 8.5	82.8 ± 1.5	2947 ± 47	105.9 ± 13.9

* Data of manufacturer of Tarnoform T300

The addition of silicone or aramid fibre does not have a substantial influence on the density of the produced composites, only the addition of thermoplastic polyurethane reduce the density by 20% which is proportional to the mass fraction.

Analysing the results from the static tensile test (Figure 1), a rise in deformations for the composition with the addition of polyurethane can be observed, as well as a reduction for this composition which is reinforced with aramid fibre while the other compositions show similar strains at break. Two tendencies can be indicated: a significant (over 30%) increase in the strength and modulus for aramid fibre-reinforced composites and a similar decrease, in particular the modulus of elasticity for the composition with polyurethane.

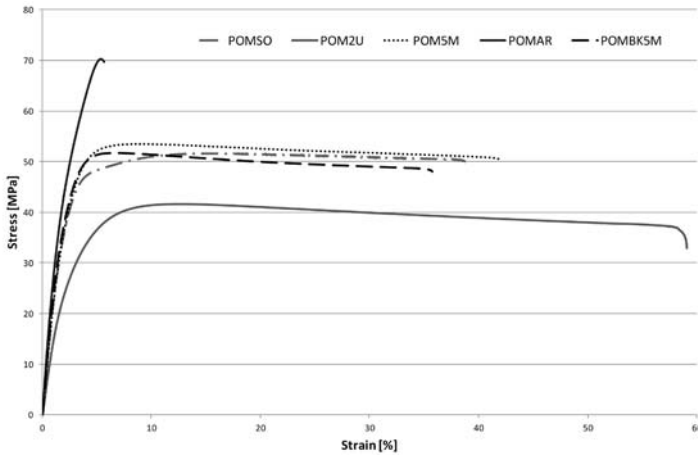


Fig. 1. Tensile stress-strain curves for the tested composites

A comparison of the static bending test's charts for the tested composites is presented in Figure 2. The curves indicate that bending properties change with a marked diminish for the composition with polyurethane. The slight variation of the module between the compositions with aramid fibre and the others compositions may indicate a lower adhesion between the aramid fibres and the polyacetal matrix.

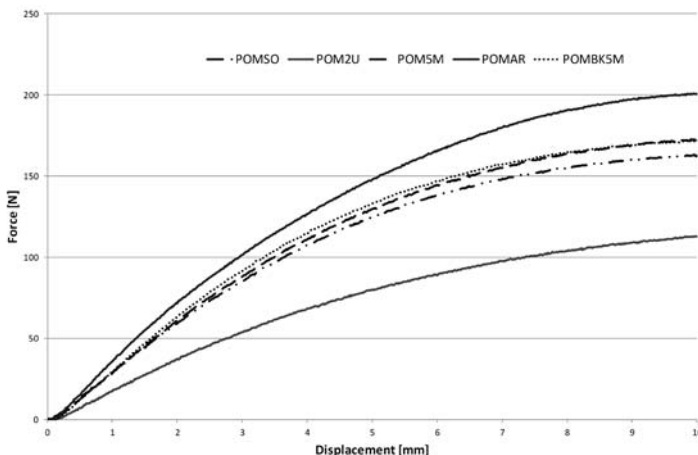


Fig. 2. Bending force-displacement curves for the tested composites

Analysis of mechanical properties at three temperatures demonstrates that the properties at lower temperature build up quite proportionally due to the fact that the glass transition temperature for polyacetal is around -50 C°. However, at elevated temperatures, a substantial stiffness-loss and a slight decline of tensile strength can be observed. The comparison is shown in Figure 3 and 4.

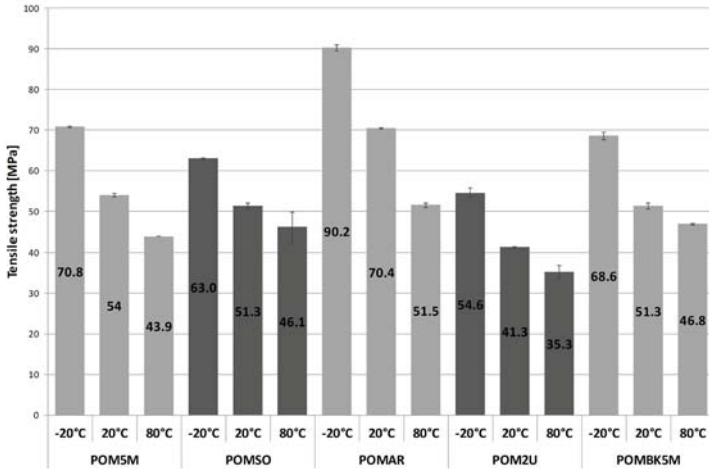


Fig. 3. The effect of temperature on tensile strength of tested composites

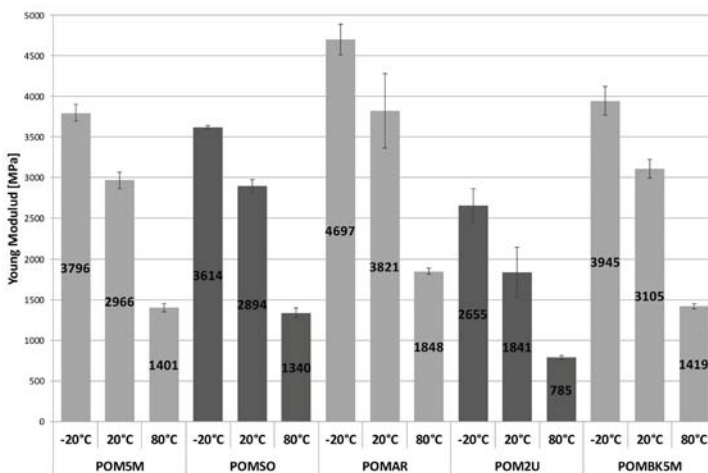
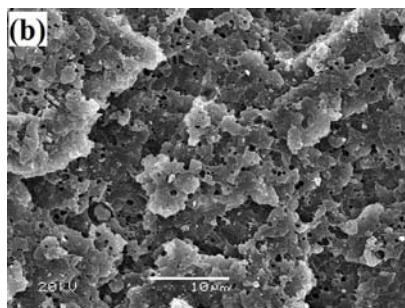
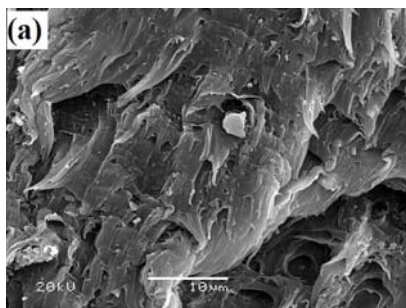


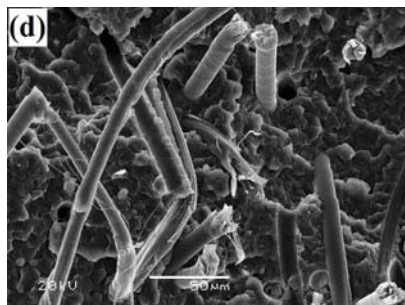
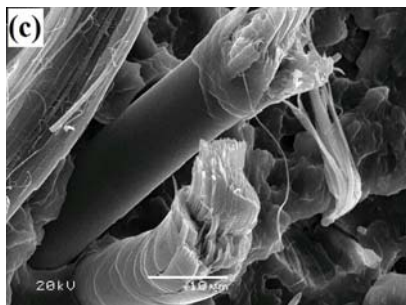
Fig. 4. The effect of temperature on tensile modulus of tested composites

It is worth noticing that the addition of siloxane oil slightly reduces the resistance to temperature. Directed measurements showed that elevated temperature lowers the possibility of strengthening the composite with aramid fibres (almost 30%), while the stiffness is still high – this is understandable due to the polymeric nature of this fibre. Conversely, in the case of a composite with the addition of polyurethane while the tensile strength slightly decreases (about 15%), the impact of elevated temperature on the tensile modulus is easily visible, a high temperature causes almost 60% diminishment in Young’s modulus. A comparison of strength and tensile modulus at reduced temperatures demonstrates a decreasing effect of reinforcement with aramid fibre. The tensile modulus and tensile strength for composition with thermoplastic polyurethane increase 44% and 30%, respectively.

POMBKSM at (a) 2000x
and (b) 1000x magnification.



POMAR at (c) 2000x and (d)
500x magnification



POMSO at (e) 2000x and (f)
1000x magnification

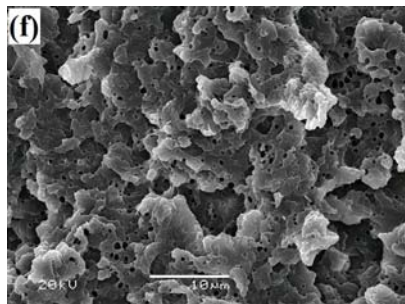
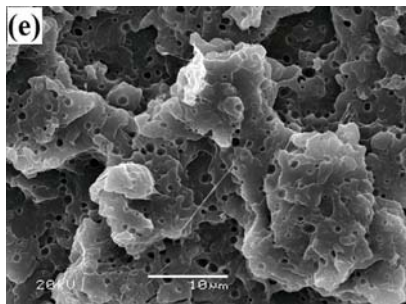
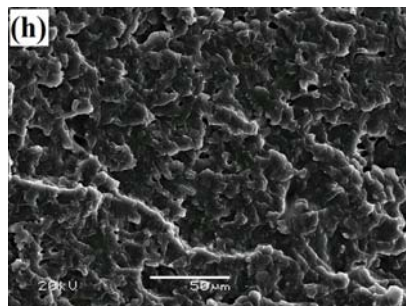
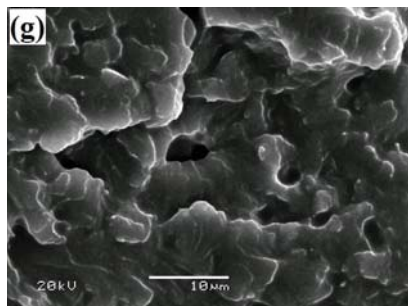
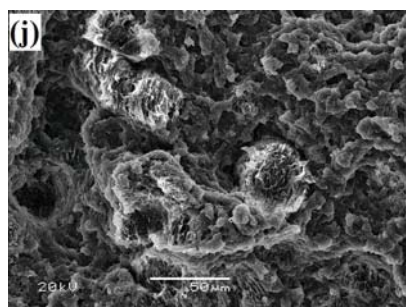
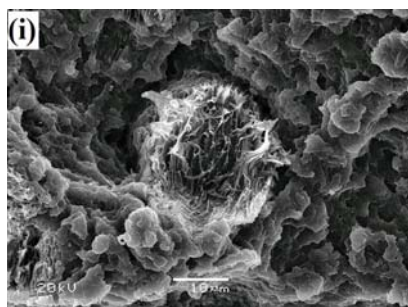


Fig. 5. SEM micrographs of tensile fractured surfaces of tested composites

POM5M at (g) 1000x and
(h) 500x magnification



POM2U at (i) 1000x and (j)
250x magnification



Cont. fig. 5. SEM micrographs of tensile fractured surfaces of tested composites

Figure 5 presents the microstructures of the tested materials. In the microstructure images of the POMBKSM composite microparticles of silicon oil (black holes with a diameter about 1–2 μm) can be observed as well as a few larger chalk particles (2–3 μm), which are evenly distributed in the polyacetal matrix. Images of POMAR show a modified polyacetal with aramid fibres. The micrographs confirm the aramid fibres with a diameter about 12.5 μm which present a well-developed surface. SEM images of POM5M show that siloxan creates small areas of crystallinity and they disperse in the form of holes with 2–6 μm in diameter. Microstructures of POM with the addition of a silicon that reduces the coefficient of friction (POMSO), create images similar to POM5M, however, the oil forms are more irregular and larger (1–4 μm). The microstructure of polyacetal with thermoplastic polyurethane (POM2U) clearly shows its two-phase nature and very good mixing of both components of the composition

4. Conclusion

The study allowed the mechanical properties of compositions based on polyacetal to be determined. The properties show that the addition of silicones cause an increase in the flexural tensile as well as a flexural and tensile modulus with a slight decrease in the tensile strength. Only the addition of aramid fibres causes an increase in tensile strength. The addition of 20% of thermoplastic polyurethane lowers tensile and flexural properties.

Comparison of the results obtained after the static tensile test at three temperatures proved that properties build up proportionally at lowered temperature and tend to slightly drop off at elevated temperatures. The addition of siloxane oil slightly reduces the resistance to temperature. Aramid fibre used as a reinforcement saves high stiffness of POM composites at elevated temperature while the addition of thermoplastic polyurethane may maintain tensile strength at an acceptable level. In the microstructure images of the POM composite with the addition of silicon irregular microparticles of silicon oil with a diameter about 1–6 μm can be observed. The microstructure of polyacetal with thermoplastic polyurethane shows its two-phase nature and the very good mixing of both components in the composition.

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