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COMPOSITES THEORY AND PRACTICE

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# EXAMINATIONS OF THE EFFECT OF MONTMORILLONITE ON SELECTED PROPERTIES AND STRUCTURE OF POLYBUTYLENE TEREPHTHALATE

**The paper discusses the results of examinations of mechanical properties and examinations of the structure of composite polybutylene terephthalate with montmorillonite. The aim of the material examinations presented in this paper was to determine the effect of the content of the fillers on the structure and properties of the polymer composite. For this purpose, the examinations of tensile strength, hardness and topography of sample surface were performed for the surface of the specimens of the composite obtained using atomic-force microscope. The specimens of composites were obtained using the injection moulding method with processing parameters for which the best properties were obtained. The study revealed an insignificant increase in tensile strength for the specimens with addition of montmorillonite of 3 and 7% from 51 MPa for butylene polyterephthalate to 53 and 54 MPa, respectively. An increase in material Shore hardness was also found. All the composite specimens were characterized by hardness at similar level of 95 to 96 degrees on the Shore scale. An increase in hardness of the composites measured by means of the ball indentation test was observed compared to polybutylene terephthalate. Addition of montmorillonite of 3 and 7% leads to the increase in hardness from 130 MPa for polybutylene terephthalate to 143 and 148 MPa, respectively. Structural changes caused by the use of montmorillonite as a filler were observed in the examinations of surface topography. Several structural drawbacks linked to the adhesion between the matrix and the filler were also found.**

**Keywords:** **polybutylene terephthalate, montmorillonite, mechanical properties, composites**

## BADANIA WPŁYWU MONTMORYLONITU NA WYBRANE WŁAŚCIWOŚCI I STRUKTURĘ POLITEREFTALANU BUTYLENU

**W artykule omówiono wyniki badań właściwości mechanicznych oraz badań struktury kompozytu politereftalanu butylenu z montmorylonitem. Celem badań materiałoznawczych było określenie wpływu zawartości zastosowanego napełniacza na strukturę i właściwości wytworzonego kompozytu polimerowego. W tym celu przeprowadzono badania: wytrzymałości na rozciąganie, twardości i topografii powierzchni próbek z wytworzonego kompozytu na mikroskopie sił atomowych. Badania przeprowadzono na próbkach kompozytów wytworzonych metodą wtryskiwania przy parametrach przetwórstwa, dla których uzyskano najkorzystniejsze właściwości. Badania wykazały nieznaczny wzrost wartości wytrzymałości na rozciąganie w próbkach z dodatkiem montmorylonitu 3 i 7% z 51 MPa dla politereftalanu butylenu do odpowiednio 53 i 54 MPa. Stwierdzono wzrost twardości wytworzonego materiału, stosując w badaniach metodę Shore'a. Wszystkie badane próbki kompozytów charakteryzowały się twardością na zbliżonym poziomie wynoszącą 95-96 stopni Shore'a. Zarejestrowano wzrost wartości twardości badanych kompozytów zmierzoną metodą wciskania kulki w porównaniu do politereftalanu butylenu. Dodatek montmorylonitu 3 i 7% powoduje wzrost twardości ze 130 MPa dla politereftalanu butylenu do odpowiednio 143 i 148 MPa. W badaniach topografii powierzchni zarejestrowano zmiany strukturalne spowodowane zastosowaniem montmorylonitu jako napełniacza. Stwierdzono pewne wady strukturalne związane z adhezją pomiędzy osnową a użytym napełniaczem.**

**Słowa kluczowe:** **politereftalan butylenu, montmorylonit, właściwości mechaniczne, kompozyty**

## INTRODUCTION

Nowadays, polymer nanocomposites play an important role. Polymer nanocomposites can be made of almost any polymer, both thermoplastic and and thermosetting. Addition of nanofillers to the polymeric matrix helps form the obtained material and modify its strength and thermal properties. Processing shrinkage of the polymeric matrix has a significant impact on properties and changes in the dimensions of products from the materials obtained [1]. The most popular nanofillers include fullerene, fullerene pipes, montmorillonite and silica. Due to low prices and high availability, silica and montmorillonite are the most often used in the industry [2-5]. The examinations performed in the study were based on the montmorillonite, which is the main component of bentonite extracted on an industrial scale in various regions of the world. However, in order to to be obtained from the fossil montmorillonite, the nanocomposite has to be modified. After its extraction, the nanocomposite is purified so that the final content of components with non-lamellar structure does not exceed 5% of volume. Large specific surface of nanocomposite, and the high cation exchange coefficient attract much interest in this material as a component of polymer nanocomposite. It is made of three-layer packages 2:1 which contain a single octahedral layer closed between two tetrahedral layers. Metal cations, especially sodium and calcium, and water particles are present between the packages. In order to ensure compatibility with the most of popular polymers, this material should be subjected to hydrophobization. This process is mainly based on exchange of metal cations into organic cations. Other compounds can also be used. This modification yields modified montmorillonite. The increased distance between packages makes it easier for the monomer and polymer particles to permeate into the interlamellar spaces. Furthermore, the material is more hydrophobic through increasing its compatibility with the most of polymers [6-8].

The aim of the examinations presented in this study was to determine the effect of the content of nanofiller in the form of montmorillonite on the structure and functional properties of the material obtained based on the polybutylene terephthalate matrix. Polybutylene terephthalate (PBT) used in the examinations is a semicrystalline polymer with high molecular mass and good processing properties. PBT is characterized by excellent resistance to the effect of a broad range of chemical substances at room temperature, e.g. aliphatic hydrocarbons, fats, petrol, oils, glycol, alcohols, carbon tetrachloride, esters and diluted acids and alkali [9-14].

## MATERIAL AND METHODS

Polybutylene terephthalate (PBT) manufactured by DuPont with commercial name of Crastin 6130 NC010 was used as a research material. The study examined specimens made of polybutylene terephthalate with 3% and 7% of montmorillonite (BYK Additives Inc., commercial name: Closite SE 3010).

The moulded pieces were obtained from Krauss Maffei KM65-160C1 injection moulding machine with a feed screw with diameter of 30 mm and L/D ratio of 23, with three zones, constant pitch over the whole length and clamping force of 650 kN. The basic conditions of specimen injection are compared in Table 1.

Strength was measured using the static tensile strength test, which enabled determination of the parameters required by the PN-EN ISO 527-2:2012 standard. Examinations were conducted using Zwick100 electromechanical strength testing machine equipped in an extensometer with accuracy of 1 μm and the measurement range of 0-100 kN. Hardness measurements were performed using the ball indentation method according to the PN-EN ISO 2039-1:2004 standard and the Shore's method according to the PN-EN ISO 868:2005 standard.

TABLE 1. **Injection moulding parameters of composite specimens**

TABELA 1. **Warunki wtryskiwania próbek kompozytów**

| Injection moulding parameter | |
|---|---|
| Nozzle temperature [°C] | 260 |
| Mould temperature [°C] | 80 |
| Injection pressure [MPa] | 130 |
| Clamping pressure [MPa] | 80 |
| Clamping time [s] | 20 |
| Cooling time [s] | 25 |

In order to map the structure of the specimens, we conducted the observation of the surface using the atomic-force microscopy (AFM). The examinations allowed for the three-dimensional visualization of the examined surfaces and evaluation of the size of selected particles of the nanofiller in the form of montmorillonite. Specimens that met the geometrical requirements of the AFM microscope were cut out and cross-sections were prepared.

Analysis of surface topography was performed using the semi-contact methodology.

The examinations allowed for the comparison of the properties and structure of PBT, PBT + 3% montmorillonite, and PBT + 7% montmorillonite.

## RESULTS AND DISCUSSION

Figure 1 illustrates example stress-strain curves for the specimens made of PBT and nanocomposites with different content of fillers. Table 2 presents the results of the tensile strength testing.

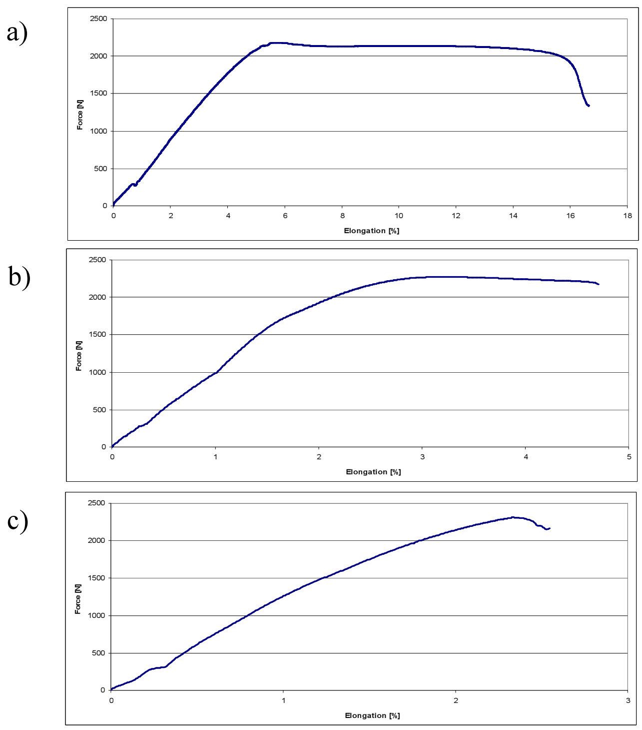


Fig. 1. Stress-strain curves for: a) PBT, b) PBT + 3% MMT, c) PBT + 7% MMT

Rys. 1. Wykresy wytrzymałości na rozciąganie: a) PBT, b) PBT + 3% MMT, c) PBT + 7% MMT

 

TABLE 2. **The results of tensile strength testing**
TABELA 2. **Zestawienie wyników badania wytrzymałości na rozciąganie**

| Specimen No. | $F_{max}$ [N] | $R_m$ [MPa] |
|---|---|---|
| 1/PBT | 2182 | 51 |
| 2/(PBT + 3% MMT) | 2273 | 53 |
| 3/(PBT + 7% MMT) | 2312 | 54 |

The static tensile strength test demonstrated that the increase in the content of montmorillonite leads to an insignificant increase in tensile strength. The highest tensile strength was observed for the PBT specimen with 7% content of montmorillonite (54 MPa). Furthermore, this value was 53 MPa for the specimen with 3% montmorillonite and 51 MPa for the non-filled PBT.

Results of hardness test evaluated using the method of ball indentation are compared in Figure 2.

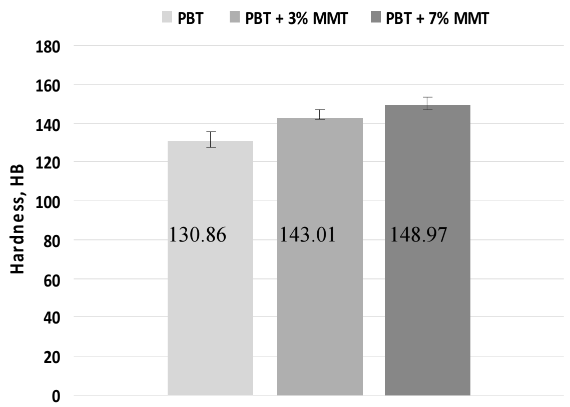


Fig. 2. Hardness measured by means of the ball indentation method
Rys. 2. Wyniki pomiaru twardości metodą wciskania kulki

Hardness testing using the ball indentation method allowed for the conclusion that the content of the nanofiller leads to the increase in hardness compared to the PBT specimen. The measurements demonstrated an insignificant effect of the nanofiller on hardness. It was found that mean hardness for pure PBT was 118 MPa, with 143 MPa for PBT with 3% montmorillonite and 148 MPa for PBT with 7% montmorillonite.

Results of hardness tests using the Shore method are presented in Figure 3.

Results of hardness based on the ball indentation method were consistent with the Shore method. Also in this case, the highest value was obtained for the PBT specimen with the content of 7% montmorillonite. Mean hardness was 90°Sh for pure PBT, 95°Sh for PBT with 3% montmorillonite and 96 ˚Sh for PBT with 7% montmorillonite. Hardness evaluated by means of the Shore method supported the tendencies for the increase in hardness of specimens with nanofiller compared to the PBT specimen. It should be emphasized that the difference in hardness in samples of 3 and 7% of nanofiller was barely 1°Sh.

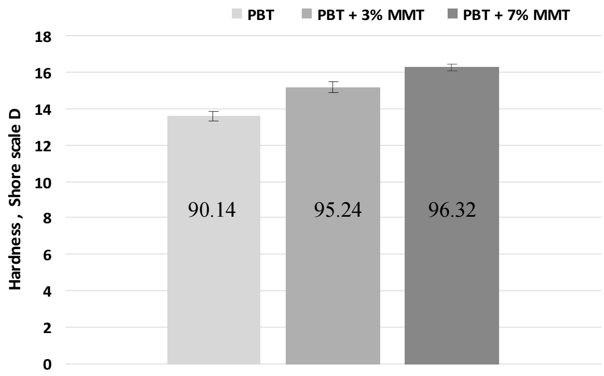


Fig. 3. Hardness measured by means of the Shore method (D scale)
Rys. 3. Wyniki pomiaru twardości metodą Shore'a typu D

The photographs that presented the surface topography are presented in Figures 4-6.

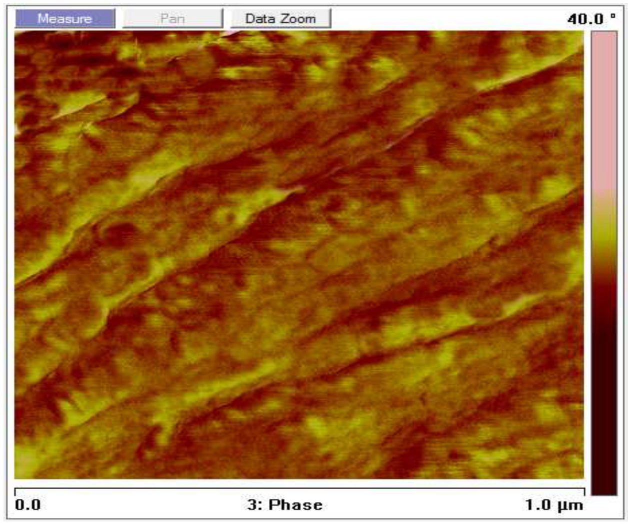


Fig. 4. AMF photographs for the surface of the PBT specimen
Rys. 4. Zdjęcia AMF powierzchni dla próbki PBT

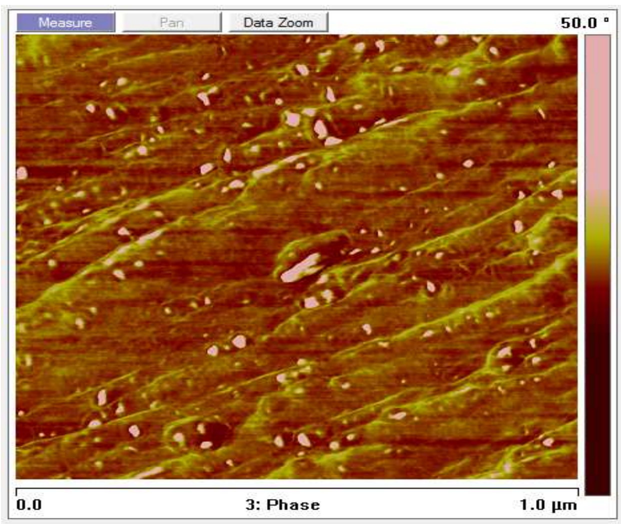


Fig. 5. AMF photographs for the surface of the PBT + 3% montmorillonite specimen
Rys. 5. Zdjęcia AMF powierzchni dla próbki PBT + 3% montmorylonitu

 

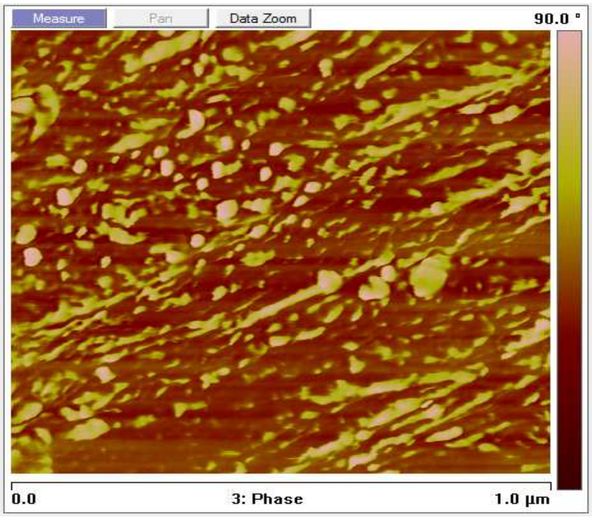


Fig. 6. AMF photographs for the surface of the PBT + 7% montmorillonite specimen

Rys. 6. Zdjęcia AMF powierzchni dla próbki PBT + 7% montmorylonitu

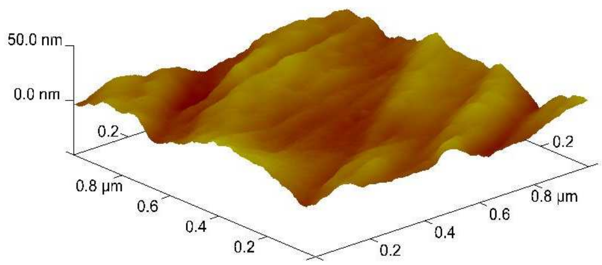


Fig. 7. 3D image for the PBT specimen, field of vision 1 µm

Rys. 7. Obraz 3D dla próbki PBT, pole widzenia 1 µm

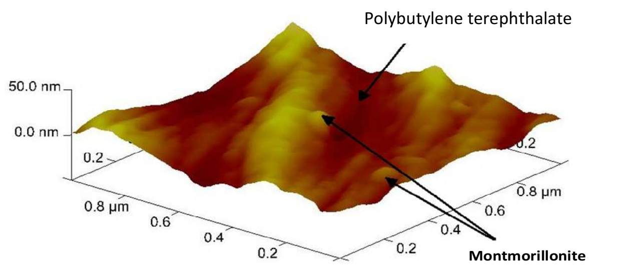


Fig. 8. 3D image for the PBT + 3% montmorillonite specimen, field of view 1 µm

Rys. 8. Obraz 3D dla próbki PBT + 3% montmorylonitu, pole widzenia 1 µm

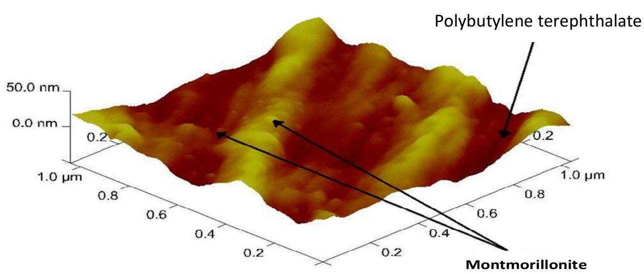


Fig. 9. 3D image for the PBT + 7% montmorillonite specimen, field of view 1 µm

Rys. 9. Obraz 3D dla próbki PBT + 7% montmorylonitu, pole widzenia 1 µm

Comparison of the size of the particles present on the surface.

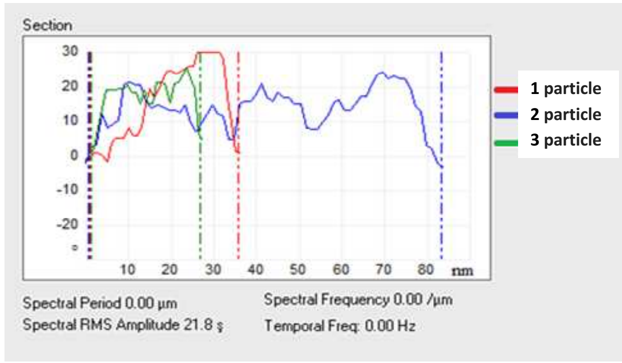


Fig. 10. Size of three selected particles of nanofillers for PBT + 3% montmorillonite

Rys. 10. Wielkość trzech wybranych cząstek nanonapełniacza dla PBT + 3% montmorylonitu

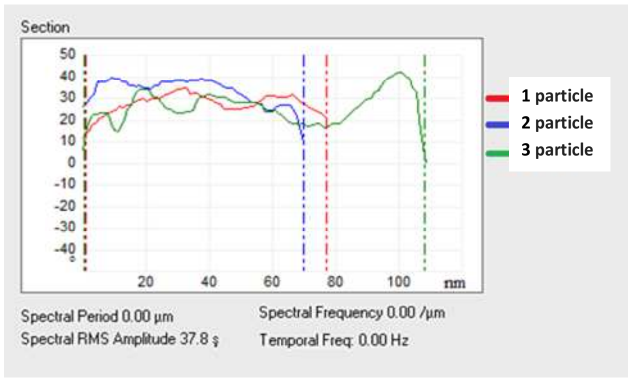


Fig. 11. Size of three selected particles of nanofillers for PBT + 7% montmorillonite

Rys. 11. Wielkość trzech wybranych cząstek nanonapełniacza dla PBT + 7% montmorylonitu

Figures 7-11 present the example size of particles for 2 specimens with the montmorillonite content. For PBT + 3% montmorillonite, the size of 3 selected particles was 27, 36 and 84 nm, whereas for PBT + 7% montmorillonite, this was 70, 78 and 108 nm. In the case of the biggest particles, they are most likely to be formed as a conglomerate of several smaller particles.

The examinations of the surface using the atomic-force microscope allowed for characterization of the microstructure of the PBT composite with nanofiller in the form of montmorillonite. The examinations demonstrated the places on the specimen's surface which suggest presence of nanofiller particles (see Figs. 5 and 6). This is also shown in Figures that illustrate 3D surface (see Figs. 8 and 9). As the filler increased, the parameter of roughness increased and he was 3.64 nm for PBT, 5.07 nm for 3% montmorillonite and 5.62 nm for 7% montmorillonite. The analysis of the particle size (Figs. 10 and 11) demonstrated that nanofiller particle size is of several ten nanometers (over 20 nm). In the case of the biggest inclusions, several maxima are noticeable in both specimens, which suggests presence of several smaller particles connected into a single conglomerate. Sizes of the fillers suggest about being agglomerates of montmorillonite, that will be suggested by AFM images.

## CONCLUSION

The findings of the study lead to the following observations and conclusions:

- An insignificant effect on tensile strength was found for addition of nanofiller in the form of montmorillonite. The values ranged from 51 MPa for PBT to 54 MPa for PBT with 7% montmorillonite.
- Addition of the nanofiller caused an increase in mean hardness measured using the ball indentation method, with 118 MPa recorded for PBT, 143 MPa for PBT with 3% montmorillonite and 148 MPa for PBT with 7% montmorillonite.
- Shore hardness measurements confirmed the tendencies for the effect of the nanofiller on hardness, whereas differences in the obtained values were much lower than it was the case for the ball indentation method.
- Mapping the surface of examined samples using the atomic force microscope confirmed the presence of montmorillonite nanoparticles in the structure.
- It was found that the nanofiller particles in the specimens had varied size (mostly over 20 nm). Conglomerates composed of several smaller particles can also be noticed. Most of particles were not bigger than 100 nm.

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