Adam Gnatowski, Mateusz Chyra
Częstochowa University of Technology, Department of Polymer Processing
Al. Armii Krajowej 19c, 42-201 Częstochowa, Poland, gnatowski@ipp.pcz.pl

THERMOMECHANICAL PROPERTIES OF POLYAMIDE 6 WITH ADDITION OF FLY ASH FROM BIOMASS

Abstract
Modification of polymer materials by various kinds of fillers is presently applied very often in massive production. This is due to the need for materials with better properties and lower prices for parts. One of the newest solutions is the filling of polymers with fly ash. This results in a change in products properties and reduction the amount of waste in the form of ashes. This article shows the results of investigations of thermomechanical properties of polyamide 6 modified by fly ash from the combustion of biomass. Comparative analysis of unfilled polyamide and polyamide composites with the addition of 5%, 10% and 15% of fly ash was performed. The specimens were obtained using injection moulding technology. The commercial name for the Polyamide 6 used in this study is TARNAMID T-27 and was manufactured by Zakłady Azotowe Tarnów. Fly ash manufactured by GDF Suez Energia Polska S.A. was applied as a filler. The investigations of mechanical properties were made using a harness by pressing ball method, impact strength by Charpy method and tensile strength. Differential scanning calorimetry (DSC), softening temperature by Vicat, and colour investigations were also performed. Pictures of microstructure were made.

Key words
Polyamide, composites, fly ash, thermomechanical properties, colour, microstructure.

Introduction

Polymeric composites are used in different industry sectors are mainly obtained using extrusion and injection technologies. The aim of filler application is to improve the mechanical, thermal and electrical properties of products compared with unfilled polymer. The reduction of mass and the price of products is also important. Fillers are most commonly used in the form of fibres and powder [1-3].

Composites on a polymer matrix are manufactured using the three methods: physical, chemical and physical-chemical. The chemical method is based on chemical reactions in polymer. The physical method is the most popular due to the easiness and the time of obtaining a composite. It consists in mixing the material with the filler. The physical-chemical is a connection of physical and chemical methods.

Various types of fillers are added to the polymeric material, including colourants, pigments and modifiers to change its thermomechanical properties or to reduce the price of the final product [4, 5]. The physical modification of thermoplastic polymers with powder or a fibrous filler leads to obtaining a new material with specific properties and structure, which can be dedicated to concrete applications, with particular focus on components used in transport, the arms industry, and the construction and automotive sectors [6].

Polyamide is a thermoplastic material. The use of thermoplastics as a composite matrix is becoming increasingly popular due to uncomplicated processing, the opportunity of longer granulate storage, and easy and fast recycling [7, 8]. Polyamide belongs to the group of nitrogen plastics. It is a structural material used for manufacturing cogwheels, bearings, and bolts. It is often modified with such additions as glass fibre or graphite. These fillers significantly improve the strength properties of the composite [9]. However, publications published over the past few years have reported the possibility of using fly ash as a filler. This gives the opportunity to obtain a cheap filler that improves the properties of the material and reduces the amount of waste from the combustion [10-12].

Currently, there is a desire to increase the amount of energy produced from renewable sources. Biomass from wood waste is increasingly used as a source of fuel. However, this causes problems with the formation of ash from combustion [13].

The aim of this study was to analyse the effect of adding fly ash from biomass to polyamide 6. TARNAMID T-27 was used as a material. The examinations of mechanical properties were made using a harness by pressing ball method, impact strength by Charpy method and tensile strength. Differential scanning calorimetry (DSC), softening temperature by Vicat and colour investigations were also performed. Microstructure was observed at a magnification of 400x.

Research methodology

The commercial name for the Polyamide 6 used in this study is TARNAMID T-27 and was manufactured by Zakłady Azotowe Tarnów. Fly ash manufactured by GDF Suez Energia Polska S.A. was applied as a filler. The ashes come from the combustion of biomass composed with 80% wood waste and 20% coconut shells. The specimens were obtained using the injection moulding technology by means of a KraussMaffei KM65-160C1 injection moulding machine. Samples were made with the following injection parameters:

- Injection pressure: 100 MPa,
- Holding pressure: 45 MPa,
- Holding time: 20 s,
- Mould temperature: 100 oC,
- Injection temperature: 280 oC,
- Cooling time 15 s.

Hardness testing was carried out using the pressing ball method. Test was carried out according with norm: PN-EN ISO 2039-1:2004. Impact strength was conducted by Charpy method in accordance with standard PN-EN ISO 179-1:2010 using the pendulum hammer 5 J. Tensile strength investigations were carried out by means of the strength testing machine Inspekt Desk 20 (Hegewald&Peschke). Test was carried out according with norm: PN-EN ISO 527-1:2012.

Differential scanning calorimetry was performed using a NETZSCH 214 Polyma machine. The specimens were weighed by means of the SARTORIUS scales with a precision of 0.01 mg, internal calibration option and closed weighing space. The mass of the specimens ranged from 7 to 12 mg. The DSC curves were recorded during heating of the specimens with a rate of 10 °C/min within a temperature range of 35 to 300°C. The crystallinity degree and value of the temperature of physical transitions were evaluated using the NETZSCH software. This software allows for the examination of the profile of the specimen melting at a given temperature range and for the determination of the surface area between the thermographic curve and the basic line in the range of endothermic reflex. The degree of crystallinity (S_k) of the filled specimens was calculated based on the following equation [14]:

$$S_k = \frac{\Delta H_m}{w_c \Delta H_K} 100\% \quad (1)$$

where:

ΔH_m – enthalpy of fusion for the material examined,

ΔH_k – enthalpy of fusion for the completely crystalline material,

w_c – mass fraction of homopolymer added to the composite examined

Test was carried out according with norm: PN-EN ISO 11357-1:2016-11.

The softening temperature by Vicat was marked on the device N8 manufactured by HAAKE method, in accordance with standard PN-EN ISO 306:2014-02

The colour of the specimens was measured using an X-Rite spectrophotometer. Test was carried out according with norm: PN-EN ISO 11664-4:2011. The examinations were carried out using the CIELAB model (Fig. 1). This model describes the colour by means of three coordinates: a, b and L. The values of a coordinate determine the colour from green to red, while the b coordinate defines the colour from blue to yellow. Parameter L (luminance) characterizes the brightness of the colour from black to white [15].

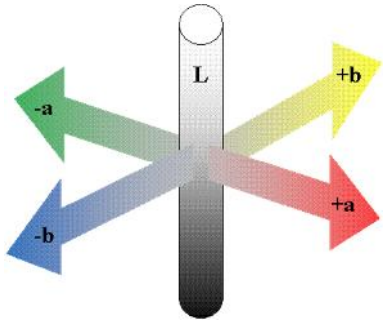

Fig. 1. CIELab space
Source: Author's

The microstructure was observed using the Nikon ECLIPSE E 200 optical microscope. The specimen's thickness ranged from 12 to 16 µm, cut out using the Thermo ELECTRON CORPORATION microtome**.**

Results and discussion of research

Results of the hardness testing are compared in Fig. 2

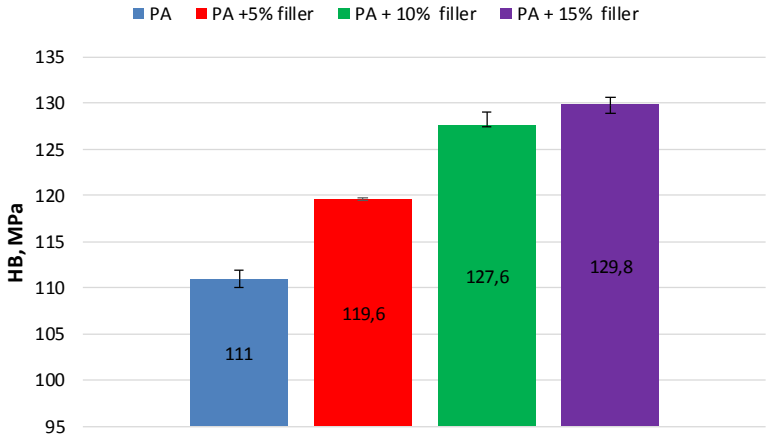

Fig. 2. Results of hardness investigations
Source: Author's

The lowest hardness was observed for the non-filled polyamide – 111 MPa. Hardness grew with the increased content of fly ash. For samples with 15% fly ash, hardness increased by 18.8 MPa in compared to polyamide without filler. In earlier carried out investigations of TARNAMID T-27 with 15% glass fibre was observed very similar results of hardness [16]. It gives information, that application of fly ashes as a filler increase of hardness of composite in the similar degree as a very popular filler which is glass fibre.

The opposite relationship was observed for the impact strength investigations, which are presented in Fig. 3. Non-filled polyamide was characterized by the highest value of impact strength. The difference of value between polyamide and composite with 15% filler is 1.84 kJ/m^2. However, the difference between composite samples is not so large. Impact strength for specimens with 5% filler is only 0.3 kJ/m^2 lower than samples with 15% fly ash.

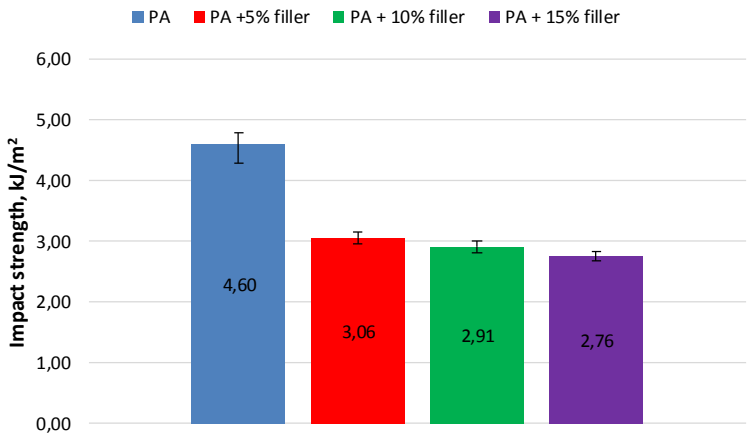

Fig. 3. Results of toughness investigations
Source: Author's

Figures 4, 5 and Table 1 illustrate the results of the tensile strength measurements.

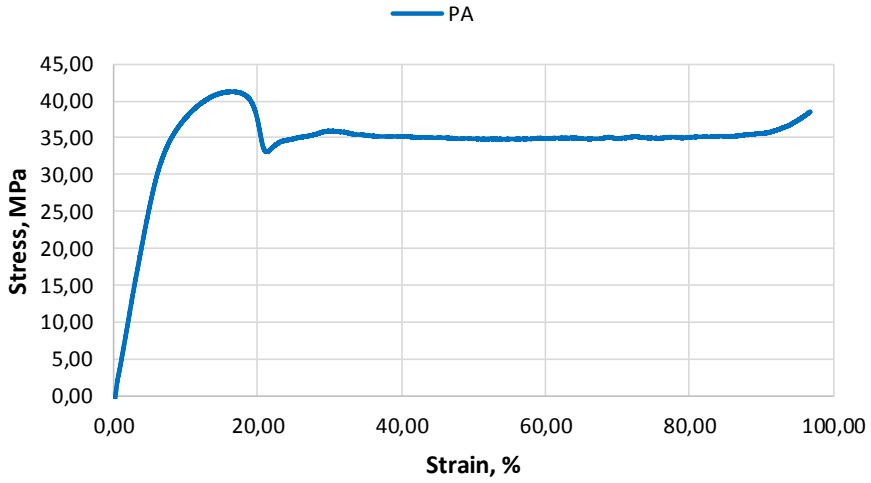

Fig. 4. Results of tensile strength investigations of polyamide
Source: Author's

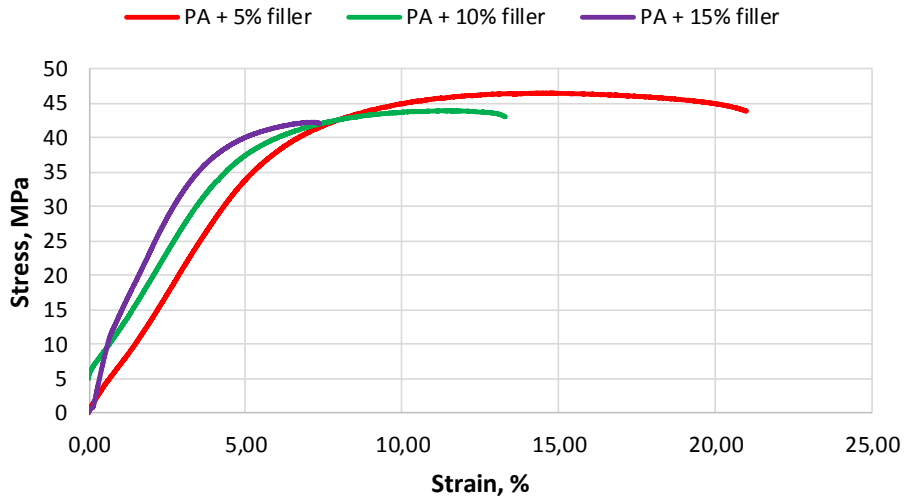

Fig. 5. Results of tensile strength investigations of composites of polyamide
Source: Author's

Tab. 1. Results of tensile strength investigations

Samples	Tensile strength [MPa]	Stress at break [MPa]	Maximum elongation [%]
PA	41	38	98
PA+5% filler	46	44	21
PA+10% filler	44	43.5	13
PA+15% filler	42	41.5	7

Source: Author's

The lowest value of tensile strength was observed for samples made from polyamide. In composite samples, there was a growth in tensile strength. However, the highest value was noticed for the composite with 5% fly ash, and further increase caused a decrease in tensile strength. As shows the previous investigations, too high content of filler can cause a decrease of tensile strength of composites. It is due by lower content of polymer matrix [17]. For the composite specimens, the maximum elongation decreased. In no-filled samples an elongation of 98% was recorded, while composite with 15% samples lengthened only 7%. Along with the increase of hardness, material become more fragile and his elongation decreases. Results obtained for differential scanning calorimetry are presented in Table 2 and Fig. 6.

Tab. 2. Results of DSC investigations

Samples	Degree of crystallinity [%]	Melting range [°C]	Max. melt temperature [°C]
PA	26.21	219.4 – 229.4	224.0
PA+5% filler	28.64	218.0 – 229.3	224.0
PA+10% filler	25.08	220.7 – 228.5	224.2
PA+15% filler	24.82	220.3 – 227.7	223.4

Source: Author's

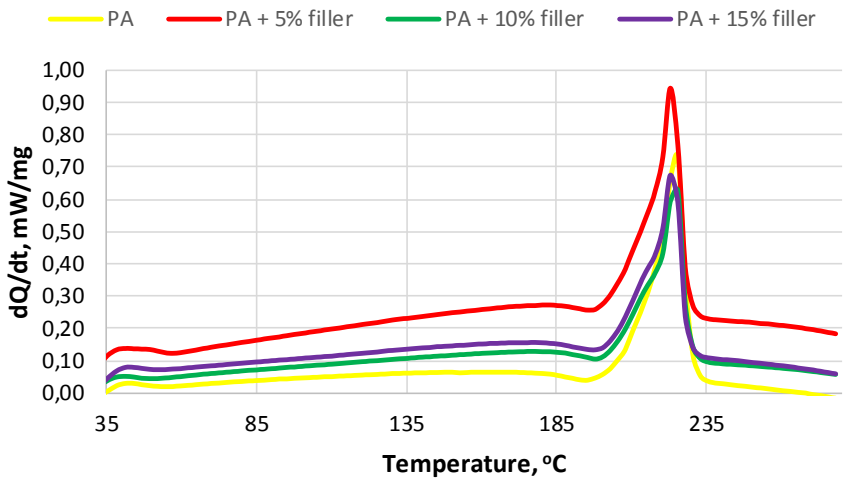

Fig. 6. Thermogram of polyamide and composites
Source: Author's

The highest degree of crystallinity was observed for polyamide with 5% fly ash. This is caused by the effect of filler, which, when cooled down, leads to the formation of the centres of nucleation, which increases content of the crystalline phase of the polymeric matrix in the composite. However, in samples with a greater degree of refill, a decrease in degree of crystallinity was observed. A small amount of filler may cause an increase in the degree of crystallinity, due to the probability of intermolecular interactions in the polymer, leading to the formation of crystallization centres upon cooling. The reason for the decrease in the value of the degree of crystallinity may be the change in structure (Fig. 10). The increase in the fly ash content may affect the orientation of the filler in samples [18]. The addition of fly ash was caused by a narrowed of range of melting temperature. The temperature with a maximum melting peak was close for each investigated sample.

Results of softening temperature by Vicat are compared in Fig. 7

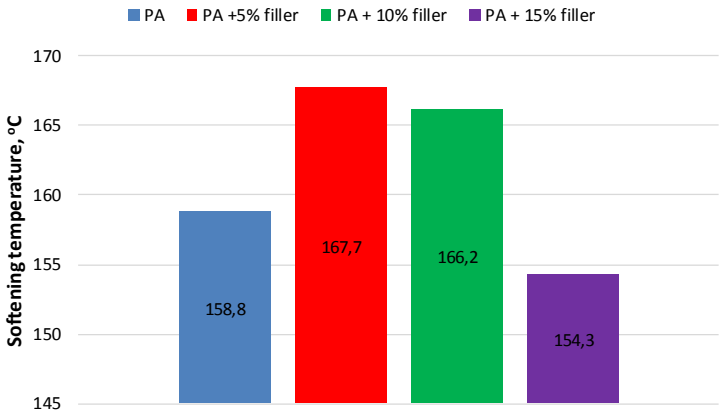

Fig. 7. Results of softening temperature by Vicat investigations
Source: Author's

The highest value of softening temperature was observed for polyamide with 5% additional filler. This represents an increase of approximately 5% compared to unfilled polyamide. Along with the increase of fly ash, there was a decrease of temperature, at which the measuring needle penetrated the 1mm in the sample. The lowest value of softening temperature by Vicat was observed for composite with 15% of filler. It is due by higher share of amorphous phase, which shows DSC investigations.

Figures 8, 9 and Table 3 present the results of colour measurement for the analysed materials.

Tab 3. Results of colour investigations

Samples	**L**	**a**	**B**
PA	61.57	-1.25	-4.8
PA+5% filler	29.03	2.13	4.36
PA+10% filler	28.72	1.93	3.55
PA+15% filler	27.84	2.13	3.94

Source: Author's

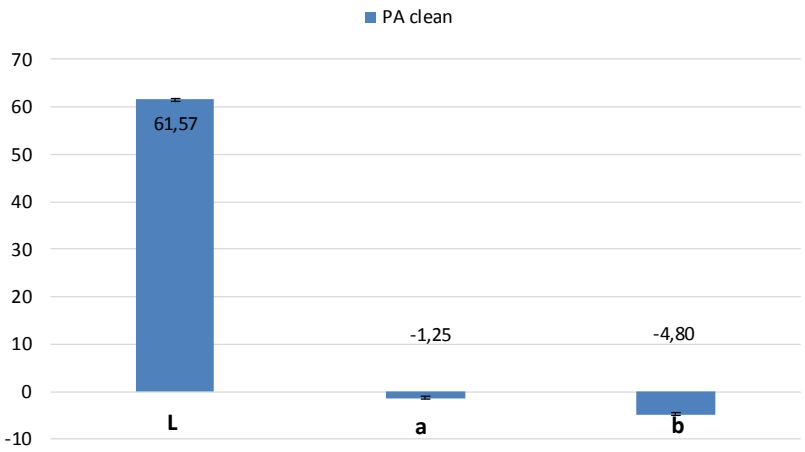

Fig. 8. Results of colour investigations of polyamide
Source: Author's

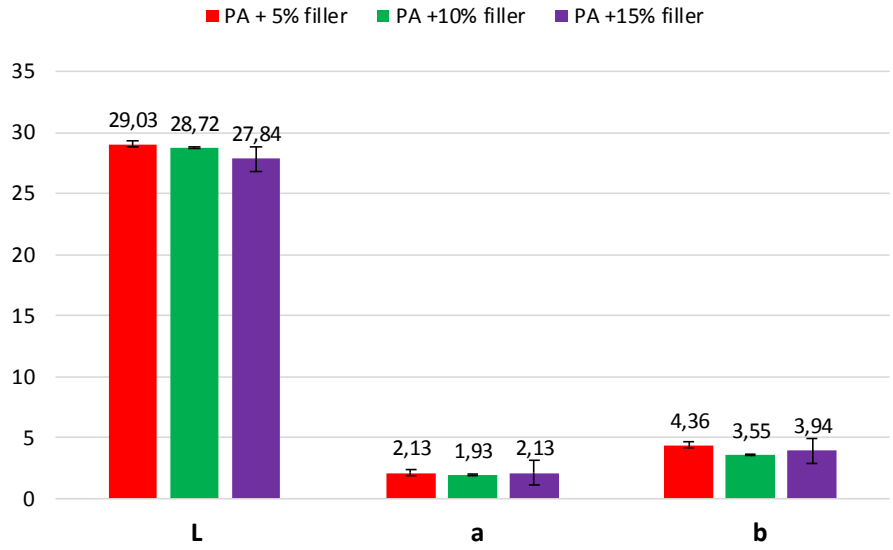

Fig. 9. Results of colour investigations of composites of polyamide
Source: Author's

In the composite samples, there was a lower value of luminance compared with non-filled polyamide. The colour of the samples with additional fly ash took on a red and yellow hue. The difference in coordinates between the filled samples are practically imperceptible.

Fig. 10 presents photographs of the microstructure of the materials studied taken at a magnification of 400x.

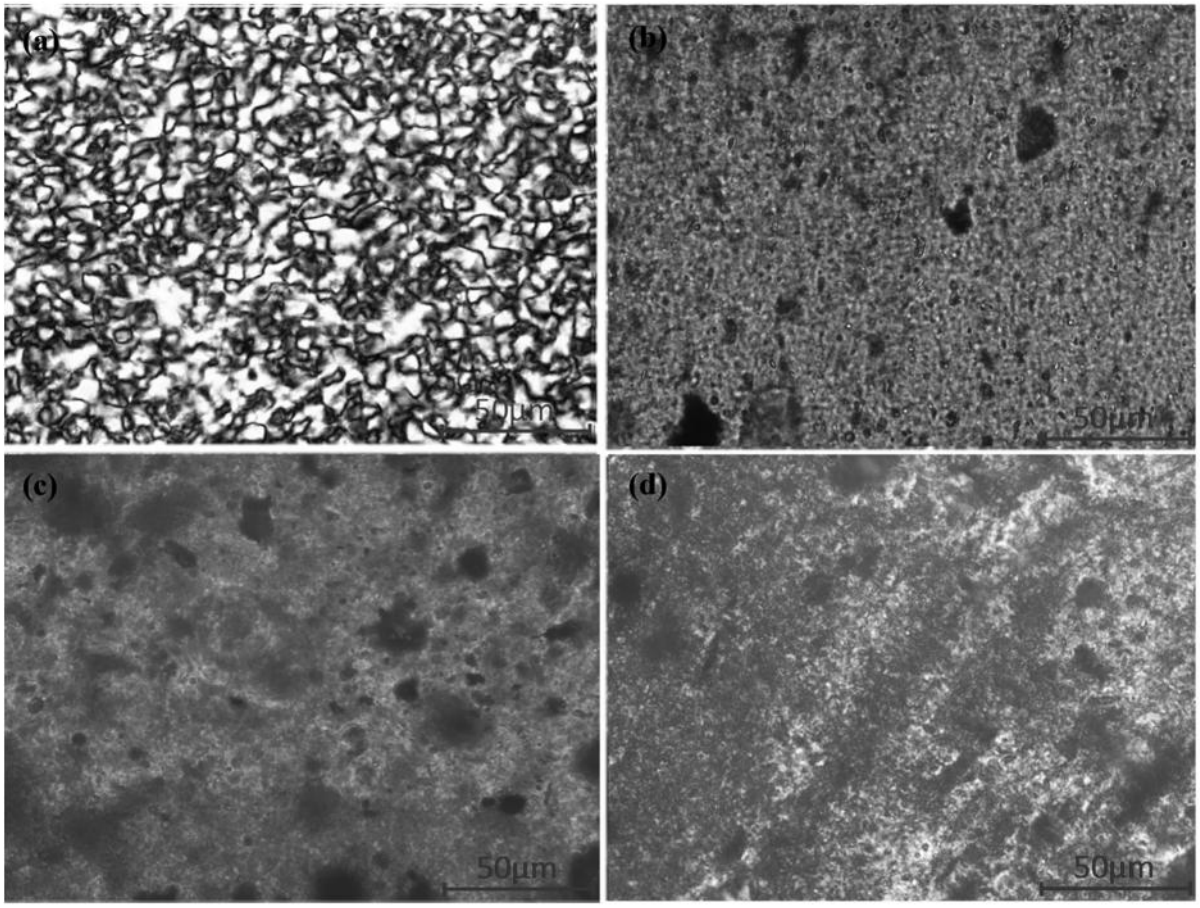

Fig. 10. Microstructure observed in magnification 400x: a) PA, b) PA + 5% filler, c) PA + 10% filler, d) PA + 15% filler
Source: Author's

A reduction in the size of spherulites was observed in the specimens with the addition of filler. Furthermore, a noticeable inclusion caused by the addition of fly ash was observed in the polymer specimens. Special defragmentation of crystallites was observed for composites with 10% and 15% additional filler.

Summary and conclusions

The addition of fly ash from biomass causes a change of thermomechanical properties compared with unfilled polyamide. Along with the increase of fly ash, there was an increase of hardness and a decrease of impact strength. The highest tensile strength was observed for a composite with 5% filler. However, composite samples were much lower in maximum elongation. The highest degree of crystallinity and of softening temperature by Vicat was observed for samples with 5% fly ash. The addition of filler had a slight impact for the value of melting temperature. Composite samples were characterized by different colour coordinates in comparison with unfilled polyamide. The defragmentation of the crystalline structure for composite samples was observed. The injection of a polyamide composite with fly ash produces composites with better properties and lower prices. The application of this filler also reduces waste derived from combustion.

References

[1] Ozimina D., Madej M.: *Tworzywa sztuczne i materiały kompozytowe*, Wydawnictwo Politechniki Świętokrzyskiej, Kielce 2010.

[2] Legocka I., Wierzbicka E., Talal M.J. Al-Zahari, Osawaru O.: *Wpływ modyfikowanego haloizytu na strukturę, właściwości cieplne i mechaniczne poliamidu 6*, Polimery, 2013, nr 1, s. 24-32.

[3] Gnatowski A.*: Influence of injection moulding condition and annealing on thermal properties, structure, colour and gloss of composite polyamide 6 with glass beads*, Composites Theory and practice, 2012, nr 2, s. 115-120.

[4] Legocka I., Wierzbicka E., Al.-Zahari T.M.J. Osawaru O., *Wpływ modyfikowanego haloizytu na strukturę, właściwości cieplne i mechaniczne poliamidu 6*, Polimery, 2013, 58, nr 1, 24-32.

[5] Hyla I., Tworzywa sztuczne, PWN, Warszawa 1984.

[6] Gnatowski A., Wawrzyniak J., Szymański D., Kula M., Wojciechowska M., *Wpływ starzenia elektrochemicznego na właściwości termomechaniczne poddanych cyklicznemu obciążaniu tworzyw polimerowych stosowanych w przemyśle motoryzacyjnym*, Przemysł Chemiczny 2014, 1(93), 79-84.

[7] Boczkowska A., Kapuściński J., Lindemann Z., Witemberg-Perzyk D., Wojciechowski S., *Kompozyty*, Wydanie II zmienione, Oficyna Wydawnicza Politechniki Warszawskiej, Warsaw 2000.

[8] Ozimina D., Madej M., *Tworzywa sztuczne i materiały kompozytowe*, Wydawnictwo Politechniki Świętokrzyskiej, Kielce 2010.

[9] Hyla I.: *Tworzyw sztuczne właściwości-przetwórstwo-zastosowanie,* Wydawnictwo Politechniki Śląskiej, Gliwice 2000.

[10] Igarza E., Pardo S. G., Abad M. J., Cano J., Galante M. J., Pettarin V., Bernal C., *Structure–fracture properties relationship for Polypropylene reinforced with fly ash with and without maleic anhydride functionalized isotactic Polypropylene as coupling agent,* Materials & Design, 2014, 85-92.

[11] Garbacz A., Sokołowska J. J., *Concrete-like polymer composites with fly ashes – Comparative study*, Construction and Building Materials, 2013, 689-699.

[12] Pardo S. G., Bernal C., Ares A., Abad M. J., Cano J., *Rheological, thermal, and mechanical characterization of fly ash-thermoplastic composites with different coupling agents,* Polymer Composites, 2010, 1722–1730.

[13] Ciesielczuk T., Kusza G., Nemś A. *Nawożenie popiołami z termicznego przekształcania biomasy źródłem pierwiastków śladowych dla gleb,* Ochrona środowiska i zasobów naturalnych, 2011, nr 49, 219-227.

[14] Balcerowiak W., *Oznaczenie stopnia krystaliczności układów polimerowych metodą różnicowej kalorymetrii skaningowej (DSC)*, Polimery, 1998, nr 6, s. 373-378.

[15] Molenda J., Wrona M., Siwiec E.: *Zastosowanie modelu CIE lab w badaniach barwy lotnych popiołów*, Problemy Eksploatacji, 2012, nr 3, s. 177-187.

[16] Bałaga Z., Biedak D., Gnatowski A., *Examinations of properties and structure of polymer Composites with quartz filler,* Composites Theory and Practice, 2015, 228-232.

[17] Gnatowski A., Chyra M., *Badania wpływu starzenia elektrochemicznego na właściwości kompozytów poliamidu z włóknem szklanym i piaskiem kwarcowym,* Przemysł Chemiczny, 2015, 103-107.

[18] Gnatowski A., Ulewicz M., Chyra M., *Analysis of Changes in Thermomechanical Properties and Structure of Polyamide Modified with Fly Ash from Biomass Combustion,* Journal of Polymers and the Environment, 2017, 1-8