KONRAD SZUSTAKIEWICZ*), MAŁGORZATA GAZIŃSKA, ADAM KIERSNOWSKI,
JACEK PIGŁOWSKI

Wrocław University of Technology
Polymer Engineering and Technology Division
ul. Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

Polyamide 6/organomontmorillonite nanocomposites based on waste materials

RAPID COMMUNICATION

Summary — The article reports research on waste polyamide 6 and organomontmorillonite nanocomposites. The composites were prepared utilizing masterbatches in a twin screw co-rotating extruder. X-ray diffraction (XRD) studies revealed the exfoliation of layered silicates in polymer matrix. Tensile tests proved that the addition of five per cent of the organomontmorillonite may be regarded as a facile and cheap approach to improve the mechanical properties of waste polyamide 6.

Keywords: polyamide 6, organomontmorillonite, nanocomposites, recycling.

NANOKOMPOZYTY POLIAMID 6/ORGANOMONTMORYLONIT OTRZYMYWANE Z MATERIAŁÓW ODPADOWYCH

Streszczenie — W artykule opisano wyniki badań nad nanokompozytami otrzymanymi z odpadowego poliamidu 6 oraz organicznie modyfikowanych montmorylonitów. Kompozyty wykonano z przedmieszek otrzymywanych w wytłaczarce dwuślimakowej współbieżnej. Badania rentgenograficzne wykazały, że delaminacja warstwowych glinokrzemianów w kompozycie jest całkowita (rys. 1—2) oraz częściowa (rys. 3) i zależy od rodzaju poliamidu użytego do wytworzenia przedmieszki. Testy wytrzymałościowe potwierdziły, że dodatek kilku procent warstwowego organomontmorylonitu do odpadu poliamidowego może być względnie prostą i tanią metodą otrzymania materiałów o bardzo dobrych parametrach mechanicznych (tabela 2).

Słowa kluczowe: poliamid 6, organomontmorylonit, nanokompozyty, recykling.

Polymer/layered silicates nanocomposites were invented in 1980s and in a short time became a subject of investigation in many research groups around the world [1]. The main advantages of nanocomposites in comparison with neat polymers are significant improvement in modulus, heat deflection temperature, permeability and retardant enhancement at low filler content (few wt. %) [2]. Nanocomposites overcome the conventional glass fiber reinforced polymers disadvantages such as high density and loss of transparency [3]. The improvement of consumer properties is observed mainly in the case of well dispersed layered silicates in the polymer matrix, so-called exfoliated nanocomposites. In this case, the size (thickness) of crystal layers is in the range of a few nanometers. The naturally occurring montmorillonites (MMT) are commercially used as the nanocomposites fillers. The main reason of that is their high availability and low price. To simplify the exfoliation of the filler in the polymer matrix, the silicates are surface treated with organic compounds. The homogeneous dispersion of unmodified clay in the polymer matrix is very difficult to achieve, because of high surface area and strong interparticular interactions [4—6]. Modification of the MMT leads to obtaining so-called organomontmorylonite (OMMT). Typically, this is accomplished by exchanging inorganic cation originally present in the galleries for organic one. As a modifiers of the montmorillonite ammonium cations containing at least one organophilic *n*-alkyl chain are generally used.

The aim of this research is to elaborate the universal method of preparation of fully exfoliated nanocomposites based on recycled polyamide 6 and organomontmorillonite with improved mechanical properties as compared to waste polyamide 6.

---

*) Author for correspondence; e-mail: konrad.szustakiewicz@pwr.wroc.pl

EXPERIMENTAL

Materials

Polyamide 6 [PA6, trade name Tarnamid T-27 with a melt volume-flow rate MVR = 120 cm^3/10 min (275 °C/5 kg) and density d = 1.14 g/cm^3] and recycled polyamide 6 (PA6R, trade name EKO BK T-30, which is a production waste), both supplied by Zakłady Azotowe Tarnów (Poland) were used.

Organically modified montmorillonites under trade name NanoBent ZW1 (cation exchange capacity CEC = 85 meq/100 g, d_{001} = 1.8 nm) and NanoBent ZW3 (CEC = 85 meq/100 g, d_{001} = 4.4 nm), both delivered by ZMG Zębiec (Poland) were used as fillers.

Preparation of nanocomposites

PA6 and PA6R were dried for 48 h at 80 °C (to the level of ~0.1 wt. % of water content in polymer) under vacuum. The organomontmorillonites were also dried for 4 h at 60 °C before compounding.

Table 1. Screw profile from hopper to die, used in experiments [the meaning of symbols characterized the pitch of the screw *e.g.* KB (5/3/45) — means kneading block with 5 disks of thickness 3 mm and staggering angle 45°; a negative pitch or angle corresponds to a left-handed element, Z8/6 — means 6 rows with 8 teeth each

Element of screw	Length, mm	Pitch, mm
Conveying	90	30
	60	20
Kneading block	30	KB (5/5/45)
	20	KB (5/3/-45)
Retaining	10	-20
Conveying	90	30
	20	20
Kneading block	30	KB (5/5/45)
	30	KB (5/5/-45)
Retaining	10	-20
Conveying	60	30
	20	20
Toothed disk	40	Z 8/6
Conveying	30	30
Kneading block	30	KB (5/5/45)
	30	KB (5/5/-45)
Retaining	10	-20
Conveying	105	30
	80	20

The nanocomposites were obtained in two steps in air atmosphere using co-rotating twin-screw extruder Brabender DSE 20/40 (D = 20 mm, L/D = 40). The screw profile is given in Table 1. Rotational speed of the screws was 250 min^{-1} and temperature range was 220—240 °C. Composites were extruded with the addition of 0.3 wt. % of thermal stabilizer (Louvinox HD-98) and 0.3 wt. % of lubricant (zinc stearate). In the first step the three masterbatches of PA6 with one of the filler *i.e.* NanoBent ZW1 or NanoBent ZW3 in amount of 30 wt. % and PA6R with 30 wt. % of NanoBent ZW1 were extruded (samples M-PA6/ZW1, M-PA6/ZW3 and M-PA6R/ZW1, respectively). In the second step the masterbatches were diluted with PA6R to obtain the final 5 wt. % of filler content [samples (PA6R + PA6)/ZW1, (PA6R + PA6)/ZW1 and PA6R/ZW1]. The extrudates were cooled down in water to 80 ± 5 °C and then pelletized. Samples for mechanical tests were injection moulded using Arburg 221 M injection moulding machine and were dried for 24 h at 80 °C under vacuum before tests. The neat PA6 and PA6R were also extruded to ensure the same thermomechanical history of all investigated samples.

Methods of testing

The mechanical properties of nanocomposites were determined according to standard PN-EN ISO 527-1, including tensile modulus, tensile strength, stress and strain at fracture with Tira Test 2705 tensile testing machine (water content in the samples was 1 ± 0.1 wt. %).

Wide angle X-ray scattering (WAXS) experiments were carried out on Rigaku Ultima IV diffractometer (Bragg-Brentano geometry) with Ni-filtered CuKα radiation generated by a sealed X-ray tube. The radiation source was powered by a generator operated at 40 kV and 30 mA. Data was collected in a step-scan mode (in 0.05°/2θ steps) within the range of 2θ from 1.1° to 10°. The basal spacing distance of the silicate layer were calculated from the estimation of (001) plane peak in X-ray diffraction (XRD) patterns using Braggs's law.

RESULTS AND DISCUSSION

The structure of composites

The structures of all composites were investigated using X-ray diffraction technique. The obtained XRD curves are shown in Figures 1—3. The scans recorded for neat organomontmorillonite and PA6R are also included for comparison. As it can be seen in Figure 1, the main diffraction maximum from the layered structure of NanoBent ZW1 is located at 2θ = 5° which corresponds to the basal spacing of the modified silicate. The value of the interlayer distance calculated according to Braggs's law equals 1.8 nm. On the diffractogram of the filler there is also a second slight diffraction peak located at 2θ = 6.2°. On the XRD pattern recorded for masterbatch M-PA6/ZW1 the maximum at 2θ = 5° dissappeared. However it can be seen slight diffraction maximum at 2θ = 2.8° and 2θ = 6.2°. This fact allows to conclude that the highly loaded composite (30 wt. %) contains the remains of non-exfoliated montmorillonite. The X-ray pattern obtained for the (PA6R + PA6)/ZW1 composite (5 wt. % of filler) indicates that the content of non exfoliated silicates is much lower in comparison with PA6/ZW1. In fact, the X-ray pattern of (PA6R + PA6)/ZW1 (in 2θ range from 1.1 to 10°) is similar to the XRD curve of unfilled PA6R. As it can be seen in Figure 2, XRD curve of NanoBent ZW3 shows three diffraction maxima 2θ = 1.7°, 2θ = 4.3° and 2θ = 6.3°. The three peaks are attributed to the layer structure of silicates. The NanoBent ZW3 contains three fractions of montmorillonites with different interlayer distances, *i.e.* d_{001} = 5.2 nm, 2.0 nm and 1.4 nm. XRD pattern of M-PA6/ZW3 shows no longer 2θ = 1.7° maximum and the others are much smaller. That fact allows to conclude, that the masterbatch contains partially delaminated organomontmorillonite. In the case of composite (PA6R + PA6)/ZW1 all diffraction maxima disappeared.

Figure 3 contains, similarly to Figure 1, XRD patterns of nanocomposites based on waste PA6R and NanoBent ZW1, however the masterbatch was based also on the waste polymer. The curves of M-PA6R/ZW1 and M-PA6/ZW1 samples, with the same filler content, are quite similar. However, for M-PA6R/ZW1 the maximum at 2θ = 5.6 o is better outlined than for M-PA6/ZW1 at 2θ = 6.2°. The XRD pattern (Fig. 3) obtained for the PA6R/ZW1 composite (after dilution the masterbatch with PA6R to filler content of 5 wt. %) indicates that exfoliation wasn't achieved (diffraction maximum located at 2θ = 6°).

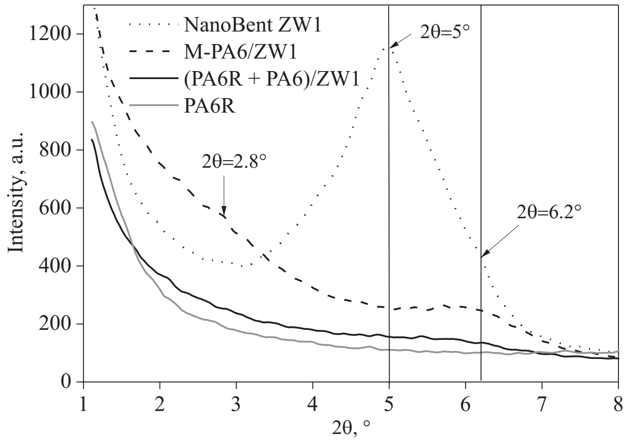

Fig. 1. XRD curves of NanoBent ZW1 filler, neat PA6R, composites M-PA6/ZW1 and (PA6R + PA6)/ZW1

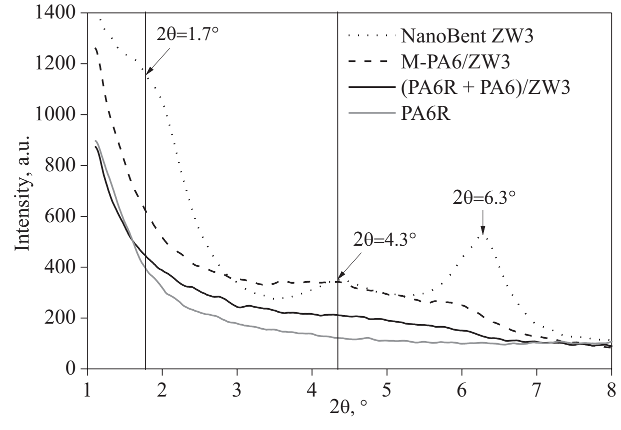

Fig. 2. XRD curves of NanoBent ZW3 filler, neat PA6R, composites M-PA6/ZW3 and (PA6R + PA6)/ZW3

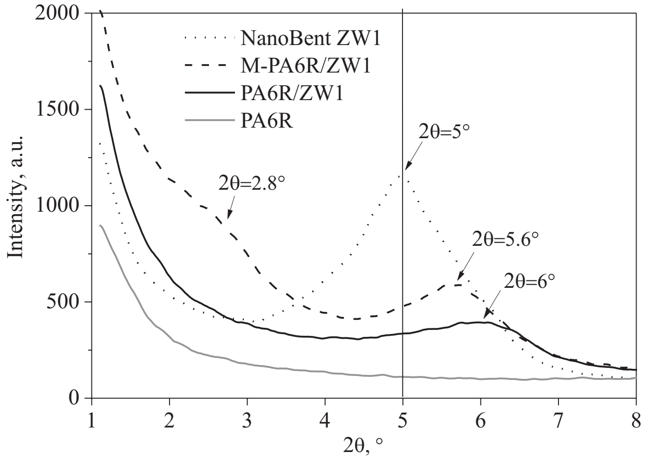

Fig. 3. XRD curves of composites M-PA6R/ZW1 and PA6R/ZW1 together with curves obtained for NanoBent ZW1 and waste PA6R

In discussed composites, good dispersion of the fillers in PA6R was achieved thanks to neat commercial PA6 used to produce the masterbatches. In the samples where the masterbatch was based on waste PA6R, the exfoliation of the fillers in the final product was not achieved. The reason of that is poor quality of waste PA6R which contains probably a small amount of other fillers, additives and polymers. PA6R can be also partially degraded during the extrusion process what results in a difference in the molecular weight distribution and viscosity in comparison to commercial PA6. To avoid the fluctuation of the composition and properties of waste PA6R, to obtain fully exfoliated composites with nanobentonites in two step extrusion, it is necessary to use commercial neat PA6 to produce masterbatch in the first step.

Mechanical properties

The mechanical properties of the neat PA6, waste PA6R and their composites with 5 wt. % of organomontmorillonites are presented in Table 2. The data analysis leads to the conclusion that independently of the type of applied filler, fully exfoliated nanocomposites obtained from masterbatch with PA6 exhibit much better mechanical properties than the neat PA6R. In fact, the tensile strength of the composites based on waste PA6R with PA6 is near to the corresponding value of neat PA6. Moreover, the Young's modulus of the composites is 15—30 %

higher than for neat PA6. The growth of stiffness causes a reduction of strain at fracture which is a disadvantage of the composites. Even though the stress at fracture is more than 25 % higher (in the case of both nanocomposites) in comparison with neat PA6.

Table 2. Mechanical properties of the PA6, waste PA6R and their nanocomposites with 5 wt. % of organomontmorillonite

Sample	Tensile strength MPa	Young's moduluIs MPa	Stress at fracture MPa	Strain at fracture %
PA6	65.5 ± 2.5	1859 ± 42	39.5 ± 2.3	45 ± 12
PA6R	41.8 ± 4.8	864 ± 84	34.9 ± 5.4	30 ± 4
PA6R/ZW1	60.0 ± 6.1	1938 ± 87	46.2 ± 7.1	12 ± 3
(PA6R + PA6)/ZW1	64.4 ± 3.5	2367 ± 82	55.3 ± 8.9	6 ± 1
(PA6R + PA6)/ZW3	62.2 ± 0.8	2133 ± 53	49.4 ± 4.4	12 ± 3

Interestingly, the values of Young's modulus and the stress at fracture of the PA6R/ZW1 composite are higher than in the case of PA6R and even than in the case of neat PA6, however not as good as in the case of both fully exfoliated (PA6R + PA6)/ZW1 and (PA6R + PA6)/ZW1 nanocomposites. Additionally, the value of the tensile strength of the PA6R/ZW1 composite is about 9 % lower than the corresponding value of the neat PA6 and 4—7 % lower than for (PA6R + PA6)/ZW1 and (PA6R + PA6)/ZW1 composite.

CONCLUSIONS

The results of investigations of polyamide 6/organomontmorillonite composites obtained in the twin screw co-rotating extruder indicate straight dependence between structure and mechanical properties of nanocomposites. To obtain composites with fully exfoliated organically modified bentonites in waste polyamide 6 matrix it is necessary to use commercial neat PA6 to produce masterbatches in the first step of that process. The second step is the dilution of prepared masterbatches by waste PA6R. Such a processing method enables to obtain exfoliated nanocomposites with good mechanical properties based on the waste polymer. The study shows that obtaining nanocomposites based on regranulate of polyamide 6 and organomontmorillonites can be an interesting recycling method for this polymer

REFERENCES

1. Okada A., Usaki A.: *Macromol. Mater. Eng.* 2006, **291**, 1449.
2. Sinha Ray S., Okamoto M.: *Prog. Polym. Sci.* 2003, **28**, 1539.
3. Le Baron P. C., Wang Z., Pinnavaia T. C.: *Appl. Clay Sci.* 1999, **15**, 11.
4. Zanetti M., Costa L.: *Polymer* 2004, **45**, 4367.
5. Oleksy M., Heneczkowski M., Galina H.: *Polimery* 2006, **51**, 799.
6. Galeski A., Piórkowska E.: *Polimery* 2007, **52**, 321.

Received 26 XI 2010.

W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— *P. Król, P. Chmielarz* — Przegląd najważniejszych metod kontrolowanej polimeryzacji rodnikowej. Cz. II. CRP z przeniesieniem atomu (ATRP) i przemysłowe wykorzystanie procesu

— *D. Pieczyńska, U. Ostaszewska, D. M. Bieliński, J. Jagielski* — Modyfikacja polimerów za pomocą bombardowania jonowego. Cz. I. Historia, aktualny stan wiedzy i perspektywy rozwoju

— *J. Lubczak* — Wielohydroksyalkilowe pochodne i polieterole otrzymywane ze związków azacyklicznych. Cz. II. Reakcje z formaldehydem i węglanami alkilenowymi (*j. ang.*)

— *M. Choczyński, B. Krajewska, Z. Stęgowski, J. Nęcki* — Emisja styrenu z pianki styropianowej i cyklopentanu z pianki poliuretanowej — pomiary i modelowanie (*j. ang.*)

— *M. Rośkowicz, T. Smal* — Trwałość kompozytów adhezyjnych Belzona 1111 i Belzona 1812 (*j. ang.*)

— *H. M. Baranowska, M. Sikora, M. Krystyjan, P. Tomasik* — Analiza powstawania i struktury podwójnych żeli skrobiowo-hydrokoloidowych na podstawie czasów relaksacji cząsteczek wody (*j. ang.*)

— *A. Tokarska* — Wodorowe uszlachetnianie ciekłych produktów pirolizy odpadowych poliolefin. Cz. I. Uszlachetnianie ciekłych produktów otrzymanych w warunkach laboratoryjnych