TECHNICAL TRANSACTIONS 8/2018
MECHANICS
DOI: 10.4467/2353737XCT.18.123.8898
SUBMISSION OF THE FINAL VERSION: 20/07/2018

Stanisław Kuciel
stask@mech.pk.edu.pl
Karolina Mazur
Institute of Material Engineering, Faculty of Mechanical Engineering, Cracow University of Technology

The effect of long-term storage on the mechanical properties of composites based on polyamide 10.10 derived from renewable sources

Wpływ długotrwałgo przechowywania na właściwości mechaniczne kompozytów na osnowie poliamidu 10.10 z surowców naturalnych

Abstract

This paper presents an investigation in which bio-based polyamide 10.10 was used as a polymer matrix. Composites were reinforced in three different ways including: 10 wt% and 30 wt% of walnut shell flour as well as 30 wt% of glass fibres. The composites were prepared by injection moulding. Mechanical properties (tensile strength (σ_t), modulus of elasticity (E_t) as well as flexural modulus (E_f) and flexural stress at 3.5% strain (σ_f)) were obtained. The mechanical data of analysis showed that tensile strength and tensile stiffness significantly decreased after four years of storage. Another state was noted for the bending module, where the decrease in value was at a level of 5% compared to results obtained immediately after injection. Additionally, SEM images were taken to assess the distribution of particles and the adhesion of fillers to the matrix.

Keywords: bio-based composite, mechanical properties, injection moulding, Hiprolon 211

Streszczenie

W artykule zostały opisane kompozyty wytworzone na osnowie całkowicie biopochodnego poliamidu 10.10 wzmocnionego zmielonymi łupinami orzecha włoskiego w ilości masowej 10% oraz 30% jak również kompozyty z dodatkiem 30% masowej ilości włókien szklanych. Zbadano właściwości mechaniczne (wytrzymałość na rozciąganie (σ_t), moduł sprężystości (E_t) oraz moduł sprężystości przy zginaniu (E_f) i naprężenie zginające przy naprężeniu 3,5% (σ_f)) wytworzonych kompozytów. Dane analizy mechanicznej wykazały, że wytrzymałość na rozciąganie oraz sztywność kompozytów po czterech latach przechowywania znacznie spadły. Jednakże zaobserwowany został niewielki spadek wartości modułu zginania na poziomie 5% w porównaniu do wyników uzyskanych dla kompozytów bezpośrednio po wtrysku. Dodatkowo w celu oceny rozkładu cząstek i adhezji napełniaczy do matrycy wykonano zdjęcia SEM.

Słowa kluczowe: kompozyty na bazie surowców odnawialnych, właściwości mechaniczne, formowanie wtryskowe, Hiprolon 211

1. Introduction

Over the last decade, the replacement of polymer matrix obtained from crude oil by bio-based matrix has seen a significant increase [1]. Due to the rapid development of the automotive industry, which is the largest consumer of polyamides, the reduction of elements made from petroleum is justified. The use of bio-based matrix is beneficial in many respects because they address the import of non-renewable feedstock sources and end of life recycling [2, 3].

Composites based on polyolefin, such as polypropylene (PP) or polyethylene (PE), which are widely used on an industrial scale, are often reinforced with conventional and heavy glass fibres [4, 5]. Although on the one hand the addition of glass fibres increases the mechanical properties of composites, on the other hand it significantly increases the density of composites, which in the case of products for the automotive component is not recommended. However, the increased usage of natural fillers is clearly observed [6]. The main advantage of bio-based additives is their low density whilst retaining excellent mechanical properties, lower price, high availability and lower abrasion during preparation and manufacturing [6, 7, 8]. In addition, the use of a bio-based matrix in combination with natural additives leads to the manufacturing of fossil- and mineral-resource-free composites which promises an advantageous eco-balance. Nonetheless, fully bio-based composites have a few disadvantages. Firstly, they have poor ability to sustain high deformation without breaking. Furthermore, the addition of natural fillers makes them difficult to manufacture because natural fillers, mainly those containing lignocelluloses, are thermally sensitive components. Additionally, they have the disadvantage of having a highly hydroscopic character in comparison to the hydrophobic polyolefin matrices, which leads to weak fibre matrix interphases [3, 4].

A lot of research has been conducted which supports to the use of polymers with natural fibres such as cellulose, hemp, flax, jute, cotton and many more [9, 10, 11, 12]. The largest problem with the use of natural fillers is their low temperature of the processing. For example, lignocellulose fillers require processing at temperatures below 200 °C [13]. However, it can be find many reports of polyamide which is reinforced with natural fibres [14, 15]. These tests are mainly carried out on bio-based polyamides, such as polyamide 10.10 (PA.10.10) or polyamide 11 (PA11) because they have generally lower melting temperatures than convectional polyamide 6 (PA6) [16].

In the work of Feldman et al., PA 10.10 fully bio-based composites reinforced with 15 wt% and 30 wt % short man-made cellulose were prepared and comparison composites were filled with 30 %wt glass fibres. The researchers evaluated the influence of compounding parameters and temperature settings on the mechanical properties. They observed significant improvements in the properties such as tensile modulus, tensile strength, notched Charpy strength, energy absorption and heat distortion temperature. The obtained results from composites made using a single-step pultrusion process were higher than composites made with the use of a two-step process [16].

In another study, Battegazzore et al. investigated composites based on PA10.10 and PA6.10 reinforcement with 10 and 20 wt% of rice-husk ash (RHA). The mechanical analysis data showed that fillers increased Young's modulus, slightly decreased the tensile strength and high decreased in strain at break. In addition, Battegazzore et al. studies are important because waste which may otherwise have constituted a source of environmental pollution was used as a filler [17].

The aim of this study was to evaluate the influence of four-year storage period on the mechanical properties of neat PA10.10 (with cross-linked additives) and its composites. The mechanical properties (tensile strength (σ_t), modulus of elasticity (E_t) as well as flexural modulus (E_f) and flexural stress at 3.5% strain (σ_f)) at -24 °C, +23 °C, +80 °C were obtained. SEM images revealed the distribution of particles and the adhesion of fillers in the matrix.

2. Methodology

A polyamide 10.10 was used as a matrix; which was obtained from raw materials of natural origin, based on castor oil. This polyamide 10.10 has been produced since 2011 by the Chinese company Suzhou Hipro Polymers under the trade name Hiprolon 211.

Hiprolon 211 is a cable type product with cross-linked additives. It is a long-chain polymer characterised by very good dimensional stability, low density and water absorption, high impact resistance and good chemical resistance.

As a fillers the following additives were used:

- walnut shell flour (REHOFIX UNG 300) supplied by J. Rettenmaier & Söhne in range of particles 40-100 μm. It is natural filler which is "ready-to-use" for extrusion facilities and injection moulding machinery,
- glass fibres (GF) delivered from Lanxess AG with a diameter of 10 μm and approx length 150 μm.

Using the polyamide 10.10 matrix, composites reinforced with 10% and 30% by mass of walnut shell particles and composites with a fibres glass additive of 30 wt %, were produced. Standard dumb-bell samples in accordance with PN-EN ISO 3167 were used in the tests, which were produced on the Engel ES 200/40 HSL injection moulding machine in Tarnow by Grupa Azoty. The parameters of the injection process were the same for all of the tested materials: injection temperature range of 190-210 °C, a screw-rotation speed of 50 rpm, an injection time of 2 s, a holding pressure time of 4s, a cooling time of 20 s, a mould temperature of 50 °C, a hydraulic back pressure of 80 MPa.

Samples, density and content of renewable sources are shown in Table 1.

Table 1.

Sample	Composition	ρ(g/cm³)	Content of renewable sources (%)
PA10.10	Polyamide 10.10	1.0340±0.1	~100
PA10.10/10WSF	Polyamide 10.10 +10 wt% walnut shells flour	1.0644±0.3	~100
PA10.10/30WSF	Polyamide 10.10 +30 wt% walnut shells flour	1.1115±0.1	~100
PA10.10/30GF	Polyamide 10.10 +30 wt% glass fibres	1.2063±0.2	~70

2.1. Mechanical properties

All tests were carried out on samples immediately after the injection process from data obtained from the work of Czarnecka and Kuciel [18] and after four years of storage at 23 °C and 65% HR.

The mechanical properties were estimated by means of a universal MTS Criterion Model 43 testing machine. The tensile test was performed with a constant cross-head speed of 10 mm/min and the elongation was evaluated using an MTS axial extensometer and crosshead displacement. The values were obtained from an average of at least five specimens. The tensile test (tensile strength (σ_t), modulus of elasticity (E_t)) according to the PN-EN ISO 527-1:1998 standard was carried out. Furthermore, tensile test was carried out at temperatures -24 °C and 80 °C by placing specimens in the temperature chamber (Instron). The values of the lowered and elevated temperatures reflected the lowest and the highest temperatures at which bio-based polyamide's composites can be used.

The flexural three-point bending test (flexural modulus (E_f) and flexural stress at 3.5% strain (σ_f)) according to the PN-EN ISO 14125:2001 standard was performed on the neat PA 10.10 and its composites (23 °C and 65%HR) with a constant cross-head speed of 5 mm/min.

The morphology of each fibres type in matrix was studied using scanning electron microscope (JEOL 5510LV low vacuum) with an accelerating voltage of 15 or 20 kV on gold-sputtered tensile-test fracture surfaces specimen.

3. Results and Discussion

Figures 1 and 2 show the tensile strength and tensile modulus of the studied composites at -24 °C, +23 °C, +80 °C after four years of storage. The best results were obtained for all composites at -24 °C and the lowest at +80 °C. The tensile strength was similar for all

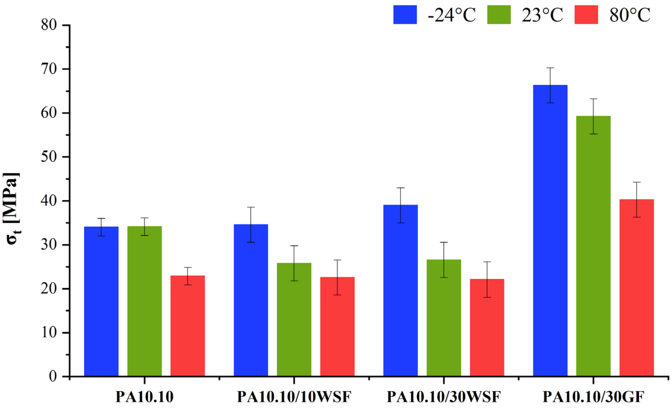

Fig. 1. Comparison of the tensile strength of neat PA10.10 and its composites at various temperatures -24 °C, 23 °C, +80 °C

composites with WSF in the range of 34-39 MPa at -24 °C. The elastic modulus for composites with WSF at -24 °C is almost tripled compared to result obtained at 23 °C and +80 °C.

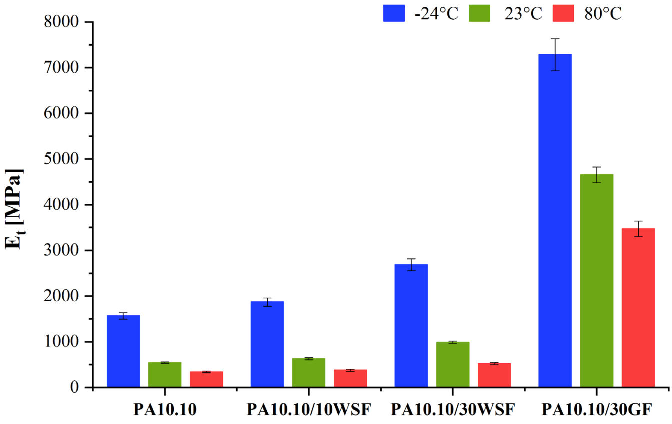

Fig. 2. Comparison of the elastic modulus of neat PA10.10 and its composites at various temperatures -24 °C, 23 °C, +80 °C

The obvious fact is that the best results were obtained for glass fibres reinforced composites. The composites have almost four-fold increase in mechanical properties compared to neat PA10.10.

Table 2. Mechanical properties of neat PA10.10 and its composites immediately after injection and after four years of storage

Temperature	**Symbol**	**σ_t [MPa]**		**E_t [MPa]**	
		after injection	**after four years**	**after injection**	**after four years**
-24 °C	PA10.10	42.1±0.4	34.00±0.3	2,131±62	1,567±54
	PA10.10/10WSF	42.9±0.4	34.55±0.4	2,599±85	1,870±103
	PA10.10/30WSF	44.1±0.3	38.95±0.4	2,599±96	2,686±93
	PA10.10/30GF	105.5±0.9	66.26±1.3	9,266±125	7,283±194
23 °C	PA10.10	29.4±0.1	34.11±0.1	658±32	541±13
	PA10.10/10WSF	26.63±0.1	25.78±0.1	800±56	627±57
	PA10.10/30WSF	28.17±0.2	26.54±0.2	1,314±78	990±67
	PA10.10/30GF	45.53±0.5	59.23±1.9	5,174±94	4,655±102
+80 °C	PA10.10	22.7±0.1	22.85±0.1	385±21	339±18
	PA10.10/10WSF	21.8±0.1	22.57±0.1	460±31	378±22
	PA10.10/30WSF	21.05±0.1	22.06±0.3	764±25	522±15
	PA10.10/30GF	39.5±0.7	40.25±1.2	4,419±31	3,471±16

A comparison of the mechanical properties of composites immediately after the injection process with composites after four years of storage is shown in Table 2. The addition of a natural filler such as WSF resulted in a significant increase in the modulus of elasticity and a slight reduction in tensile strength with increasing fibre content at all temperatures. Research conducted by Feldman and Bledzki and the results of Battegazzore et al. mentioned above show similar relationships. The authors argue that the cause of this is a higher ability to transfer stresses by particles [16, 17]. The obtained results are characteristic for composites with the addition of lignocellulosic particles [19, 20]. For composites filled with WSF, both strength and modulus values decreased after four years of storage for all temperatures. This is most probably associated with the breakdown of lignocellulosic particles.

Not surprisingly, the best results for both the elasticity modulus and strength were obtained for the composites reinforced with GF at all temperatures. This is due to the excellent mechanical properties of these fibres and the additional special fibre treatment that results in better adhesion to the matrix [21].

A surprising phenomenon is that there may only be a slight decrease in the strength properties of the composites immediately after injection at 80 °C, which is due to the partial activation of the cross-linking agent after an hour of heating in the thermal chamber. The long-term storage for four years resulted in a very similar effect of activation of the cross-linking agent. This resulted in a slight increase in tensile strength after four years with a significant 20% reduction in the modulus of elasticity. At room temperature, the cross-linking agent in time increased the strength of the composites, and the second ageing process probably caused the disintegration of the long-chain polyamide and the lowering of its stiffness.

Table 3. Bending properties of the neat PA10.10 and its composites after injection and after 4 years of storage

Symbol	σf [MPa]		Ef [MPa]	
	after injection	after four years	after injection	after four years
PA10.10	29±0.1	23±0.1	482±22	480±21
PA10.10/10WSF	59±0.2	27±0.1	581±28	581±25
PA10.10/30WSF	76±0.4	35±0.3	921±56	910±55
PA10.10/30GF	163±1.2	94±0.8	4,151±120	4,252±131

In table 2 was shown a comparison of the mechanical properties of the bending test immediately after injection and after four years of storage. For the neat PA10.10, an insignificant decrease in bending strength was obtained. However, for all composites over two-fold decrease was observed. With regard to the modulus of elasticity, the decrease in value was at a level of 5% compared to the results obtained immediately after injection.

Composite materials require strong adhesion between phases and uniform distribution of all components in the matrix to obtain composites with satisfactory mechanical properties. SEM images were used to characterize the morphology of individual fillers of composites and to assess their dispersion in the matrix as well as interfacial interactions between matrix and fillers. Figure 3 a–d shows SEM images of the tensile fracture specimens.

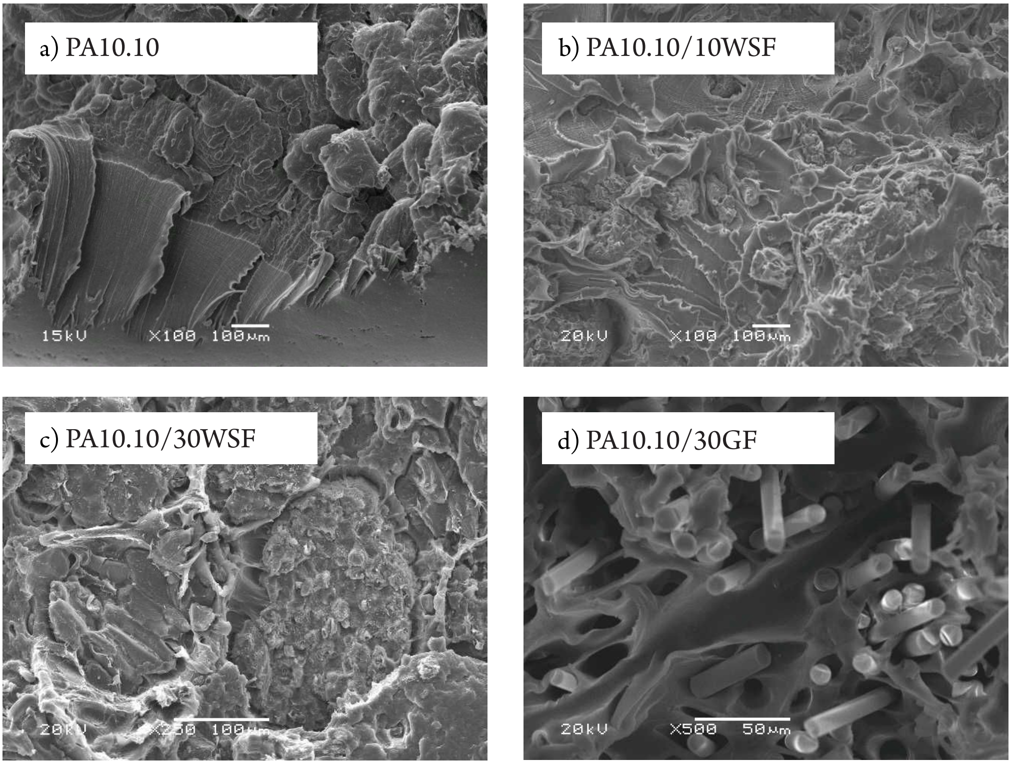

Fig. 3. SEM images of microstructure of PA10.10 composites a) neat, b) with 10 %wt of walnut shell flour, c) with 30 %wt of walnut shells flour, d) with 30 %wt of glass fibres

As can be seen in Figure 3a, neat PA10.10 is characterized by high plasticity of the breakthrough. In the Figure 3b, can be observed very well dispersed walnut shell particles in the polyamide matrix. In Figure 3c, it can be observed numerous and very regularly dispersed walnut particles in the polymer matrix, the breakthrough after fracture is characterized by brittleness. Clearly, empty places with a very small cross-section testify to the small adhesion of the nut shell particles to the resin. Figure 3d shows a fragment of a plastic fracture after fracturing with clearly cracked glass fibres partially embedded in the polymer matrix.

4. Conclusion

As a result of the tests, it was found that the properties of the cross-linking agent contained in Hiprolon 211 are much lower or no longer active after long-term storage. For all temperatures (-24 °C, 23 °C and 80 °C), the strength and the Young's modulus decreased. It can be concluded that materials of this type cannot be used for responsible parts of finished products but only for less-responsible parts with a short period of use, such as sports shoes or household appliances. The use of this type of material is possible using, for example, hybrid materials, such as combinations of biocomponents with conventional materials. Hiprolon

211 has been used in the last few years for the production of cable shields for the automotive industry, althought it has currently been replaced by another product from the 10.10 polyamide group which is also manufactured from renewable raw materials.

References

[1] european-bioplastics.org/market (access: 24.05.2018).

[2] Vold J.L., Ulven C.A., Chisholm B.J., *Torrefied biomass filled polyamide biocomposites: mechanical and physical property analysis,* Journal of Materials Science, 2015, 725–732.

[3] Espinach F.X., Delgado-Aguilar M., Puig J., Julian F., Boufi S., Mutjé P., *Flexural properties of fully biodegradable alpha-grass fibers reinforced starch-based thermoplastics,* Composites Part B: Engineering, 2015, 98–106.

[4] Oliver-Ortega H., Granda L.A., Espinach F.X., Delgado-Aguilar M., Duran J., Mutjé P., *Stiffness of bio-based polyamide 11 reinforced with softwood stone ground-wood fibres as an alternative to polypropylene-glass fibre composites,* European Polymer Journal, 2016, 481–489.

[5] Alves C., Ferrão P.M.C., Silva A.J., Reis L.G., Freitas M., Rodrigues L.B., Alves D.E., *Ecodesign of automotive components making use of natural jute fiber composites,* Journal of Cleaner Production, 2010, 313–327.

[6] Heitzmann M.T., Veidt M., Ng C.T., Lindenberger B., Hou M., Truss R., Liew C. K., *Single-Plant Biocomposite from Ricinus Communis: Preparation, Properties and Environmental Performance,* Journal of Polymers and the Environment, 2013, 366–374.

[7] Bledzki A.K., Reihmane S., Gassan J., *Thermoplastics reinforced with wood fillers: a literature review,* Polymer Plastic Technolgy Engineering, 1998, 451–468.

[8] Velthoven J.L.J., Gootjes L., Noordover B.A.J., Meuldijk J., *Bio-based, amorphous polyamides with tunable thermal properties,* European Polymer Journal, 2015, 57–66.

[9] McHenry E., Stachurski Z.H., *Composite materials based on wood and nylon fibre,* Composites Part A: Applied Science and Manufacturing, 2003, 171–181.

[10] Sui G., Fuqua M.A., Ulven C.A., Zhong W.H., *A plant fiber reinforced polymer composite prepared by a twin-screw extruder,* Bioresources Technology, 2009, 1246–1251.

[11] Orue A., Eceiza A., Arbelaiz A., *Preparation and characterization of poly(lactic acid) plasticized with vegetable oils and reinforced with sisal fibres,* Industrial Crops and Products, 2018, 170–180.

[12] Awal A., Rana M., Sain M., *Thermorheological and mechanical properties of cellulose reinforced PLA bio-composites,* Mechanics of Materials, 2015, 87–95.

[13] Nguyen T., Zavarin E., Barral II E.M., *Thermal analysis of lignocellulosic materials. Part I. Unmodified materials,* Journal of Macromolecular Science Part C Polymer Reviews, 1981, 1–65.

[14] Zierdt P.,Theumer T., Kulkarni G., Däumlich V., Klehm J., Hirsch U., Weber A., *Sustainable wood-plastic composites from bio-based polyamide 11 and chemically modified beech fibers,* Sustainable Materials and Technologies, 2015, 6–14.

[15] Duigou L., Bourmaud A., Gourier C., Baley C., *Multi-scale shear properties of flax fibre reinforced polyamide 11 biocomposites,* Composites: Part A, 2016, 123–129.

[16] Feldmann M., Bledzki A.K., *Bio-based polyamides reinforced with cellulosic fibres – Processing and properties,* Composites Science and Technology, 2014, 113–120.

[17] Battegazzore D., Salvetti O., Frache A., Peduto N., De Sio A., Marino F., *Thermo-mechanical properties enhancement of bio-polyamides (PA10.10 and PA6.10) by using rice husk ash and nanoclay,* Composites: Part A, 2016, 193–201.

[18] Czarnecka S., Kuciel S., *Polyamides composites with nanosilver particles for medical application*, Bachelor's thesis, Cracow University of Technology, 2014.

[19] Gordobil O., Delucis R., Egüés I., Labidi J., *Kraft lignin as filler in PLA to improve ductility and thermal properties,* Industrial Crops and Products, 2015, 46–53.

[20] Elanchezhian C., Ramnath B.V., Ramakrishnan G., Rajendrakumar M., Naveenkumar V., Saravanakumar M..K., *Review on mechanical properties of natural fiber composites Materials Today: Proceedings,* 2018, 1785–1790.

[21] Sanjay M.R., Arpitha G.R., Yogesha B., *Study on Mechanical Properties of Natural - Glass Fibre Reinforced Polymer Hybrid Composites: A Review*, Materials Today: Proceedings, 2015, 2959–2967.

If you want to quote this article, its proper bibliographic entry is as follow: Kuciel S., Mazur K., *The effect of long-term storage on the mechanical properties of composites based on polyamide 10.10 Derived from renewable sources* , Technical Transactions, Vol. 8/2018, pp. 167–176.