TECHNICAL TRANSACTIONS 1/2019
MECHANICS
DOI: 10.4467/2353737XCT.19.013.10053
SUBMISSION OF THE FINAL VERSION: 14/11/2018

Anna Kufel orcid.org/0000-0002-5104-0630
Stanisław Kuciel orcid.org/0000-0001-9244-7499
stask@mech.pk.edu.pl
Institute of Material Engineering, Faculty of Mechanical Engineering, Cracow University of Technology

Composites based on polypropylene modified with natural fillers to increase stiffness

Kompozyty na osnowie polipropylenu modyfikowane naturalnymi napełniaczami w celu zwiększenia sztywności

Abstract

Composites based on a polypropylene matrix with coffee ground powder, wood flour and tuff of a mass weight of 12.5wt% were produced by the method of injection moulding. Tests of tensile and bending strength properties were carried out and Charpy impact was determined at three temperatures: -24°C, 22°C and 80°C. Scanning electron microscopy (SEM) images were taken to assess the effects of reinforcement and homogenization of mixtures and to determine the characteristics of the microstructure. Composites with 12.5wt% coffee ground powder, wood flour and tuff were characterized by an increase the elastic modulus. Tensile strength slightly decreased for composites with ground coffee grains and tuff.

Keywords: polypropylene, natural fillers, mechanical properties, composites

Streszczenie

Wytworzono kompozyty na osnowie polipropylenu modyfikowane zmieloną kawą, mączką drzewną oraz tufem w ilości masowej 12.5%. Kompozyty zostały wytworzone metodą formowania wtryskowego. Została wykonana statyczna próbę rozciągania oraz zginania, a także próba udarności w trzech temperaturach eksploatacji: -24°C, 22C°, 80°C. W celu określenia charakterystyki i zbadania wpływu wzmocnienia oraz homogenizacji mieszaniny wykonano zdjęcia na skaningowym mikroskopie elektronowym. Kompozyty z 12.5wag.% zawartością kawy, mączki drzewnej lub tufu charakteryzują się zwiększonym modułem sprężystości oraz nieznacznym spadkiem sztywności dla kompozycji z kawą i tufem.

Słowa kluczowe: polipropylen, napełniacze naturalne, właściwości mechaniczne, kompozyty

1. Introduction

Natural resources are increasingly used as reinforcements of thermoplastic polymers and provide an excellent alternative to synthetic fibres [1]. Natural raw materials added to polymeric materials increase the modulus of elasticity, which leads to increased stiffness of the products made on this basis. One of the problems of using natural fillers is their low compatibility with hydrophobic polymer matrices. To improve the adhesion between the hydrophilic fibres and the hydrophobic matrix, the fibres are usually surface-modified (silanization) or compatibilizing agents are added to the polymer matrix [2]. Polypropylene products are currently used in almost all fields. Polypropylene (PP) has become a widely used polymer material that possesses low density, but high thermal stability as well as a low cost of production.

Natural fillers (lignocellulosic and mineral) such as jute [3], abaca [4], kaolin [5], talc [6] etc. are commonly used to reinforce the polymer. One natural filler is volcanic tuff, which is a compact, porous sedimentary rock and consists of pyroclastic material, often with an admixture of another clastic material cemented with a siliceous or loamy binder. Tuff is a hard rock with a high porosity, and therefore has a relatively low density. It consists of aluminium, silicon, oxygen, potassium and trace amounts of carbon. The addition of tuff (3–5%) for recycled thermoplastic polymers becomes the mixing promoter that facilitates their processing and increases their deformation capacity and the stiffness of such mixtures [7]. Studies of composites based on thermoplastics using tuff as a filler have shown that such composites are characterized by higher rigidity and surface hardness; furthermore, they have a higher temperature resistance [8]. Tuff in quantities from 10wt% to 30wt% can be used to reduce material costs by replacing more expensive admixtures such as pigments, flame retardants and impact modifiers [9].

Coffee is one of the most consumed beverages in the world. In literature, there are different research papers focused on using spent coffee grounds (SCG). The research showed that adding SCG into a polypropylene matrix promotes a slight decrease in flexural strength and restricts deformation due to stress concentration phenomena provided by dispersed particles in the PP matrix. The flexural modulus increases as a consequence of the remarkable decrease in deformation ability [10].

Currently, there are numerous combinations of agricultural by-products used as fillers (such as coconut shell, rattan, durian seed, rice hush, banana fibre) [11]. Chun et al. [12] examined the utilization of cocoa pod husk (CPH) in polypropylene biocomposites. The increase in the CPH content decreased the tensile strength and the elongation at break of PP/CPH biocomposites but increased the tensile modulus. The addition of a compatibilizer improved the tensile strength and tensile modulus of PP/CPH biocomposites. In another study [13] it was found that SCG particles have a positive effect on the matrix (PP) properties, while these performances were improved by using a chemical treatment (silane, SESB-g-MA) resulting in stronger interactions with the matrix.

Compared with traditional glass fibre and mineral fillers, wood/natural fibre fillers are less expensive, lighter, sustainable, and less abrasive to processing machines. Natural fibre composites may substitute PP- short glass fibre composites when a reduction in strength is acceptable. Wood plastic composites, on the other hand, may replace PP–talc composites, in applications where impact strength is not critical [14].

The aim of the study is to introduce natural fillers to the polypropylene matrix to increase stiffness, to change the colour and also, in the case of coffee, give a natural fragrance. For this purpose, three types of composite were produced by the injection moulding process to evaluate changes in strength properties in a wide temperature range as well as the influence of water absorption. In addition, the microstructure of the fillers and their effects on the polymer matrix were also evaluated.

2. EXPERIMENTAL PART

2.1. Materials

The polypropylene (PP) Moplen HP500N from Basell Orlen Polyolefins, Plock, Poland was used as a matrix. Tuff, wood flour and coffee ground were used as fillers. The particles of tuff (Filipowice mine, Poland) with a range of 5–20 μm were obtained by grinding on a Retsch ZM 200 mill. After grinding, the tuff was rinsed in 1molar hydrochloric acid and then calcined at 800°C. Ground coffee from grains (Tchibo Arabica – Guatemala Grande) were roasted at 250°C. The grains were ground using a Retsch ZM 200 mill to a grain size of 2–8 mm. Wood flour (Lignocel BK40/90), supplied by J. Rettenmaier & Söhne, with a fibre length of approximately 150 μm and a beam diameter of 20–30 μm, was used. As a compatibilizer, anhydride maleic PP SCONA TPPP 9112 GA (MAPP) supplied by Byk (Altana Group) was used. The standard dumbbell composites were previously mixed in a twin-screw co-rotating extruder and subsequently subjected to injection moulding. The samples (Fig. 1) were made by injection moulding on the Engel ES200/40 HSL machine at Zaklady Azotowe S.A in Tarnow (Poland). Table 1 shows the injection parameters of the produced composites in terms of temperature and injection speed.

Table 1. Injection parameters of the prepared composites

Sample	C1, °C	C2, °C	C3, °C	Nozzle temperature, °C	Holding time, s	Cooling time, s	Injection speed, mm/s	Injection pressure, bar	Injection time, s
PP	180	185	190	195	40	10	20	80	2.87
PP12M	175	180	185	190	40	10	15	80	3.38
PP12T	185	185	190	190	40	10	18	80	4.63
PP12K	175	180	185	187	40	10	17	80	3.69

Fig. 1. Injection moulded samples with ground coffee grains, wood flour and tuff

2.2. Methods

The density of the materials was measured by a hydrostatic method. The mechanical properties were estimated by a tensile test with an universal testing machine Criterion 043 with an MTS axial extensometer. Tests for tensile modulus, tensile strength and strain at break were carried out according to the EN ISO 527 standard. The test speed was set to 10 mm/min. The three point flexural test was also conducted for the compositions according to PN-EN ISO 178. Flexural modulus and flexural strength were determined. The Charpy impact test (PN-EN ISO 179-1:2010) was carried out on unnotched specimens using a Zwick HIT5.5P. Fractured surfaces from impact tests were observed by scanning electron microscopy (SEM) in a JEOL JSN5510LV. Before observation, samples were covered with a thin layer of gold. To assess the influence of water absorption,all compositions were tested in a conditioned state and after 30 days of soaking in water. Measurements of water absorption were taken after an incubation period of 1, 7, 14 and 30 day/s.

3. EXPERIMENTAL PART

The tested materials are described in table 2 with the results of the density measurements. The fillers were introduced in the amount of 12.5wt%. The introduction of natural fillers in the amount above 10% usually results in improved strength parameters and gives favorable aesthetic effects. Furthermore, the high content of fillers also contributes to the increase of water absorption and the acceleration of aging processes. The addition of wood flour, coffee or tuff did not have a significant effect on the density of the obtained composites. The highest increase in density was observed for PP12M.

Table 2. Compositions of manufactured samples with their density

Samples	Composition	Density, g/cm^3
PP	Polypropylene (Moplen HP500N)	0.909 ± 0.002
PP12M	Polypropylene + 12.5wt% wood flour + 5wt% MAPP	0.946 ± 0.002
PP12K	Polypropylene + 12.5wt% ground coffee grains + 5wt% MAPP	0.932 ± 0.001
PP12T	Polypropylene + 12.5wt% tuff + 5wt% MAPP	0.948 ± 0.005

Analysing the results from the static tensile test (Table 3), it can be observed that the elastic modulus increased for all compositions. The best result was obtained by the composition with wood flour, for which the elastic modulus at room temperature increased by over 40% and the tensile strength increased by approximately 5%. The addition of 12.5wt% tuff and ground coffee grains led to respectively 5.8% and 3.5% increase in stiffness and a slight decrease in tensile strength (4.5% and 13.5%). Analysing the results from the static tensile test at the extreme operating temperatures of -24°C and 80°C; the tensile strength was higher at the lower temperature and the lowest at the highest temperature. The same tendency was indicated for elastic modulus. The addition of powder fillers led to lower impact strength.

Table 3. Mechanical properties of the tested samples

Samples	Temperature, °C	Tensile strength, MPa	Young modulus, MPa	Strain at break, %	Charpy impact strength, kJ/cm^2
PP	-24	52.5 ± 0.1	4837 ± 81	8.8 ± 1.3	22.1 ±2.1
	22	31.0 ± 0.2	1691 ± 30	>200	unbroken
	80	21.1 ± 0.5	817 ± 64	>200	unbroken
PP12T	-24	42.9 ± 2.3	4898 ± 24	2.2 ± 0.3	6.8 ± 1.7
	22	29.6 ± 0.4	1789 ± 20	16.9 ± 4.6	10.5 ± 2.3
	80	18.5 ± 0.8	784 ± 7	28.7 ±2.8	26.5 ± 1.8
PP12M	-24	53.3 ± 0.8	5754 ± 217	2.6 ± 0.3	9 ± 0.7
	22	32.8 ± 0.1	2414 ± 106	8.80 ± 0.4	14.3 ± 0.8
	80	22.6 ± 0.5	1291 ± 51	10.9 ± 2.0	28.2 ± 0.4
PP12K	-24	37.7 ± 2.7	4526 ± 184	1.6 ± 0.2	4.7 ± 0.9
	22	26.8 ± 0.8	1756 ± 52	10.6 ± 1.4	6.6 ± 1.0
	80	18.3 ± 0.5	746 ± 30	19.1 ± 3.4	25.4 ± 7.7

Figures 2 and 3 compare the flexural test results of PP and its composites at temperatures of -24°C +22°C and +80°C. The best results of flexural modulus were obtained at -24°C and led to an increase of over 50% compared to 22°C. The best flexural strength and modulus results were obtained for PP12M composites (with wood flour). This is probably related to the good adhesion of the filler to the matrix. The lowest results were recorded for PP12K composites – with ground coffee.

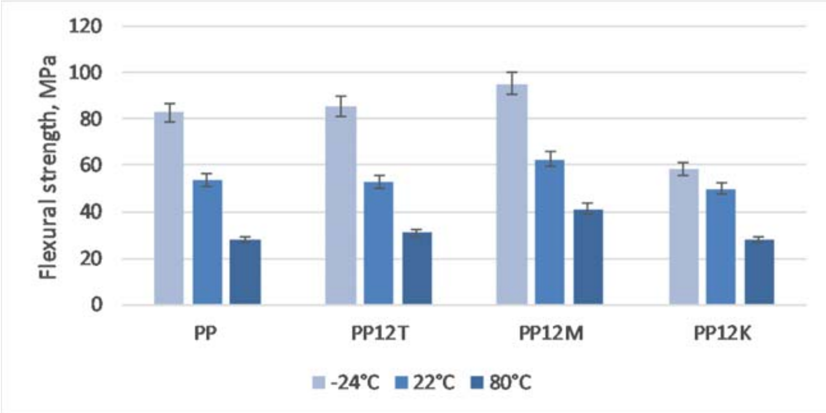


Fig. 2. The effect of temperature on flexural strength of tested composites

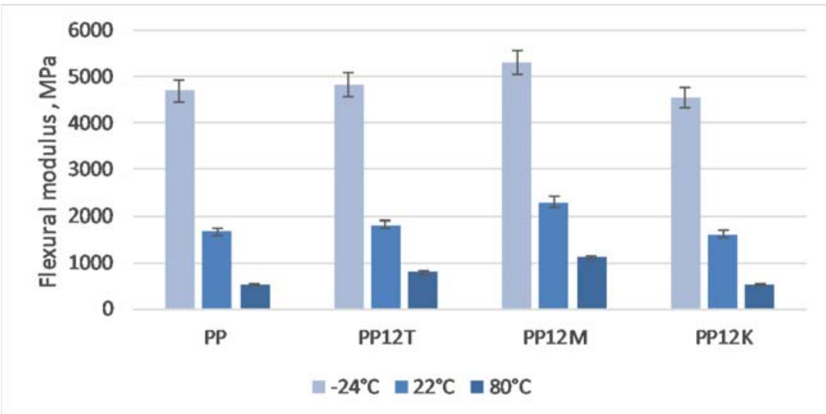


Fig. 3. The effect of temperature on flexural modulus of tested composites

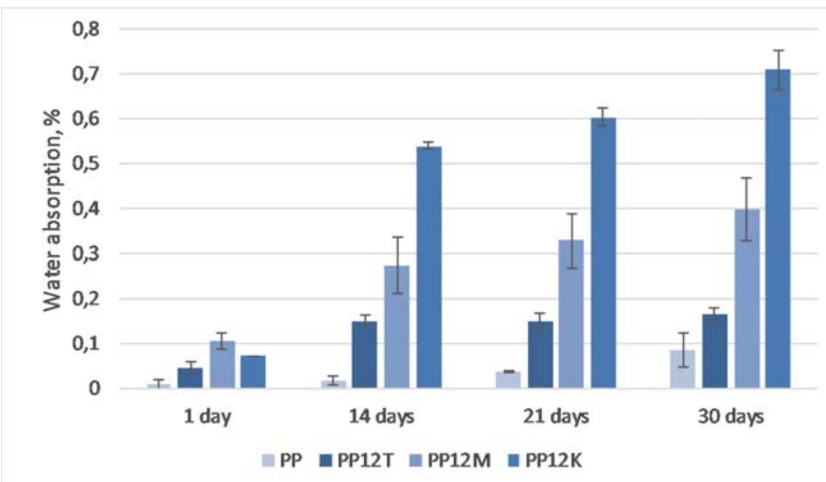


Fig. 4. Water absorption measured for the tested materials after 1, 14, 21 and 30 day/s of incubation in water

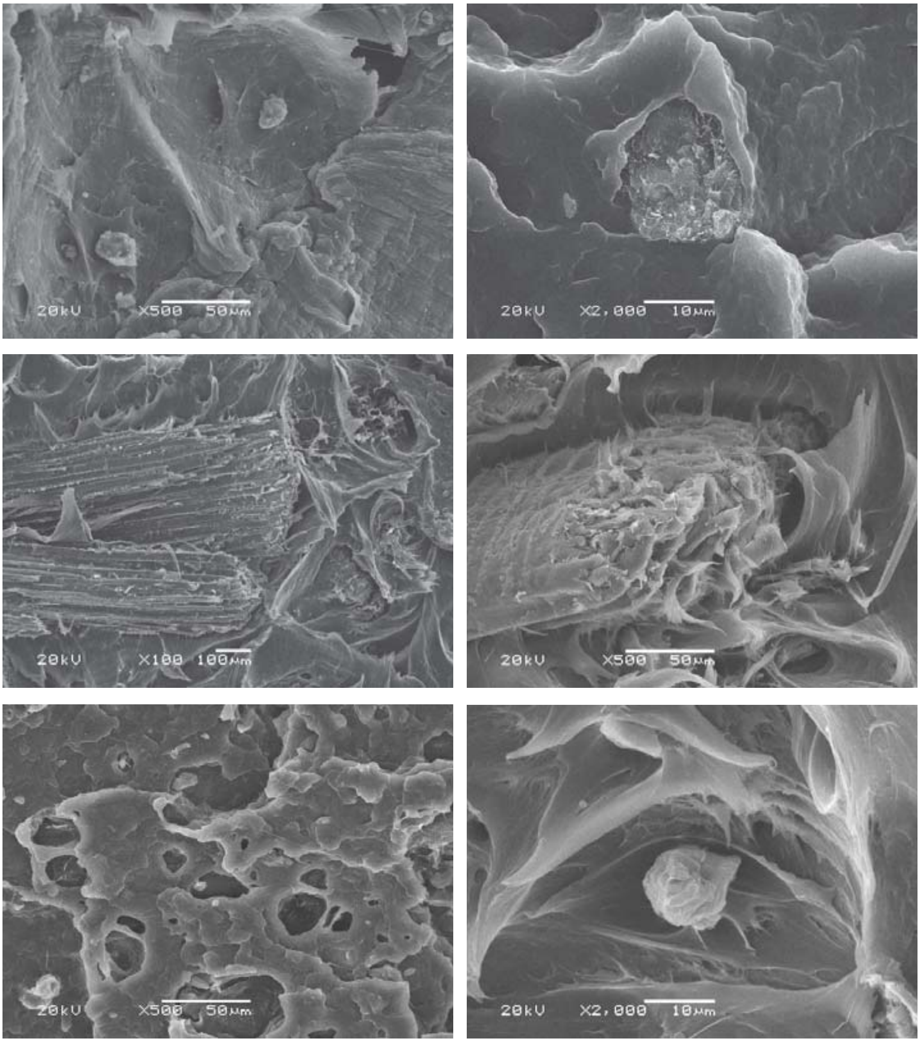
The addition of natural fillers, especially lignocellulose, increased the water absorption of all manufactured composites (Fig. 4). Initially, the composite with wood flour had the highest water absorption, however, after a few days the coffee composition absorbed the most water, probably due to the numerous micropores formed in this composite after the injection process, due to the evaporation of the remaining water from the coffee particles.

Table 4 presents the mechanical properties for the composites in the conditioned state and after incubation in water. After 30 days of incubation in water there was no significant effect on the strength properties. The tensile strength slightly decreased and the elastic modulus increased, especially for the composite containing wood flour. This phenomenon is known for lignocellulosic fillers. Slow soaking of water increased their volume and, consequently, shear stress occurred at the filler-polymer matrix border which led to an increase in stiffness. Hydrolytic degradation caused quite a significant decrease in strain at break, probably due to sorption on grain boundaries or composite fibres.

Table 4. Comparison of the mechanical properties of the samples in the conditioned state and after 30 days of incubation in water

Samples	Tensile strength, MPa		Young modulus, MPa		Strain at break, %	
	Conditioned state	After incubation	Conditioned state	After incubation	Conditioned state	After incubation
PP	31.0 ± 0.2	32.8 ± 0.3	1691 ± 30	1920 ± 26	>200	>200
PP12T	29.6 ± 0.4	26.5 ± 1.1	1789 ± 20	2131 ± 109	16.9 ± 4.6	5.6 ± 0.1
PP12M	32.8 ± 0.1	34.5 ± 0.5	2414 ± 106	2704 ± 52	8.80 ± 0.4	7.5 ± 0.9
PP12K	26.8 ± 0.8	26.9 ± 1.7	1756 ± 52	1762 ± 35	10.6 ± 1.4	9.6 ± 1.2

Figure 5 presents the microstructures of the tested materials. Tuff particles (5–20 μm) can be observed as well as ground coffee grains (2–8 mm). We can also see characteristic wood fibrils. Much smaller tuff particles with a developed surface are well embedded in the polymer matrix. Coffee particles have a diversified morphology and size and exhibit a limited adhesion to the polymer matrix.



a)

b)

c)

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

4. CONCLUSIONS

It is possible to produce good quality composites with both natural mineral and lignocellulosic fillers. The addition of ground coffee, wood flour or tuff increases the modulus of elasticity. Due to the small amount of fillers and their form (powder fillers – not fibrous), the effect of strength increase was not expected, but an improvement of stiffness was possible. Furthemore, the use of tuff to increase stiffness, gives an interesting green colour to applications and, as well as the addition of wood flour, increases resistance to aging or wear. In addition, the modification of the composite with natural fillers, facilitates the use of recyclates and the tuff, which is protected by a patent, is an addition which favors their mixing abilities.

References

[1] Saba N., Jawaid M., Alothman O.Y., Paridah M.T., *A review on dynamic mechanical properties of natural fibre reinforced polymer composites,* Construction and Building Materials, vol. 106/2016, 149–159.

[2] Yatigala N.S., Bajwa D.S., Bajwa S.G., *Compatibilization improves physico-mechanical properties of biodegradable biobased polymer composites,* Composites Part A: Applied Science and Manufacturing, vol. 107/2018, 315–325.

[3] Righetti B., Mello R., Benedetto D., Hirayama D., De Andrade O., M*anufacturing and Characterization of Jute / PP Thermoplastic Commingled Composite 2. Experimental Procedures,* Materials Research vol. 20/2017, 458–465.

[4] Vilaseca F., Valadez-Gonzalez A., Herrera-Franco P.J., Pèlach M.À., López J.P., Mutjé P., Bio*composites from abaca strands and polypropylene. Part I: Evaluation of the tensile properties,* Bioresource Technology, vol. 101/2010, 387–395.

[5] Zago D.M., Jikan S.S., Badarulzaman N.A., Nuhu A.H., E*ffect of Additives on Polypropylene / Kaolin Composite Prepared via In-situ Process,* Journal of Science and Technology, vol. 9/2017, 19–23.

[6] Qiu F., Wang M., Hao Y., Guo S., *The effect of talc orientation and transcrystallization on mechanical properties and thermal stability of the polypropylene/talc composites,* Composites Part A: Applied Science and Manufacturing, vol. 58/2014, 7–15.

[7] Kuciel S., Kuźniar S., Mikuła J., *Tuf – nowy mineralny kompatybilizator recyklatów PHED przeznaczonych do wytwarzania wyrobów metodą rozdmuchiwania,* Przetwórstwo Tworzyw, 2013, 250–258.

[8] Żmudka S., Budniak I., Kuciel S., Mikuła J., *Ocena możliwości zastosowań wulkanicznego tufu jako napełniacza polimerów termoplastycznych,* Czasopismo Techniczne, 1-M/2009, 421–428.

[9] Tarverdi P. K., Madoyan Z., *Preparation and properties of polypropylene and pa 6 composites reinforced with armenian tuff stone,* European Scientific Journal, vol. 2/2014, 161–166.

[10] García-García D., Carbonell A., Samper M.D., García-Sanoguera D., Balart R., *Green composites based on polypropylene matrix and hydrophobized spend coffee ground (SCG) powder,* Composites Part B: Engineering, vol. 78/2015, 256–265.

[11] Nikmatin S., Syafiuddin A., Hong Kueh A.B., Maddu A., *Physical, thermal, and mechanical properties of polypropylene composites filled with rattan nanoparticles,* Journal of Applied Research and Technology., vol. 15/2017,386–395.

[12] Chun K.S., Husseinsyah S., Osman H., *Utilization of cocoa pod husk as filler in polypropylene biocomposites: Effect of maleated polypropylene,* Journal of Thermoplastic Composite Materials, vol. 28(11)/2015, 1507–1521.

[13] Essabir H., Raji M., Laaziz S.A., Rodrique D., Bouhfid R., el kacem Qaiss A., T*hermo-mechanical performances of polypropylene biocomposites based on untreated, treated and compatibilized spent coffee grounds,* Composites Part B: Engineering, vol. 149/2018, 1–11.

[14] Sobczak L., Lang R.W., Haider A., *Polypropylene composites with natural fibers and wood – General mechanical property profiles,* Composites Science and Technology, vol. 72(5)/2012, 550–557.

If you want to quote this article, its proper bibliographic entry is as follow: Kufel A., Kuciel S., *Composites based on polypropylene modified with natural fillers to increase stiffness,* Technical Transactions, Vol. 1/2019, pp. 187–196.