ANIMAL SCIENCE AND GENETICS
Published by the Polish Society of Animal Production
vol. 18 (2022), no 3, 57-67
DOI: 10.5604/01.3001.0016.0365

Research Article ***Open Access***

Production of biodegradable packaging with sheep wool fibres for medical applications and assessment of the biodegradation process

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SUMMARY

The aim of the study was to design and produce composite packaging using sheep wool fibre. An important aspect was the development of fully biodegradable and thermally insulated packaging as an ecological alternative to commonly used packaging materials such as expanded polystyrene. The samples were produced by injection moulding and examined under a digital microscope. The surface wettability and wetting angle were measured with a goniometer; surface roughness was measured with a Hommel Tester T1000 profile meter using a TH300 sensor and a filter according to ISO 11562; and infrared spectroscopy analysis was carried out on a Bruker Tensor 27 spectrometer. To evaluate biodegradability, four samples were placed in soil in an ageing chamber with two ultraviolet lamps with an intensity of 35 W/cm^2 for 48 h. Then the samples were taken from the soil and washed with distilled water. One hour in the ageing chamber approximates 5,645 hours of exposure to natural solar radiation, and thus 48 h was equivalent to 30 years. They were examined under a digital microscope and with a goniometer, and they were tested for thermal insulation over 20 h. The composite packaging showed similar thermal insulation characteristics to those of expanded polystyrene packaging. The addition of wool fibre caused the wetting angle value to increase. Surface roughness increased considerably with the wool content of the samples. No new chemical bonds are formed in the material, as the IR spectrum was unchanged (for the wool fibre composites, peaks were observed to be at the same locations as for pure polylactide samples). The introduction of wool fibres accelerated the biodegradation process.

KEY WORDS: sheep wool, biocomposite, thermally insulated boxes

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Received: 24.04.2022 Received in revised form: 12.09.2022
Accepted: 15.09.2022 Published online: 16.09.2022

INTRODUCTION

The ongoing development of civilization, demographic changes, and increasing environmental pollution caused by polymeric materials motivate the introduction of biodegradable modifiers and raw materials (e.g. natural fibres) in materials engineering. A particularly important group in materials engineering is composites, with a wide range of properties and environmental impacts (Blicharski, 2001). Together with polypropylene, polyethylene, poly (vinyl chloride) and poly(ethylene terephthalate), polystyrene currently accounts for 71% of global production, of which polyolefines account for as much as 46%. Over the last eight years the demand for plastics by the packaging industry has increased by as much as 60% (Kozera-Szałkowska, 2019). A Plastics Europe report found that the packaging industry takes the lead in plastics use at 39,9%. The demand for plastics by European Union converters is 51,2 million tonnes, while the collected plastic waste in the same year was 29,1 million tonnes, of which only 32,5% was recycled, 42,6% was used for energy recovery, and as much as 24,9% is stored in landfills (https://www.plasticseurope.org). To safeguard the natural environment, there is growing interest in the use of natural fibres as modifiers in biodegradable composites (Chandramohan and Marimuthu, 2011). Wool fibre is distinguished by unique physicochemical properties such as high thermal insulation value; therefore, it can be used as a component of biocomposites, in line with the strategies of bioeconomy and sustainable development (Molik and Potocka, 2019). Wool fibre products can increase hydrophobicity and exhibit good insulation properties, and they are biodegradable. The aim of the study was to design and produce composite packaging using sheep wool fibre. An important aspect of the study was the development of a fully biodegradable and thermally insulated packaging material as an ecological alternative to commonly used packaging materials. It was designed for application in the medical and pharmaceutical sectors.

MATERIAL AND METHODS

The thermally insulated and biodegradable packaging was made with the wool of Polish Mountain Sheep (white and black fibres) kept at an experimental station of the Department of Animal Nutrition and Biotechnology, and Fisheries, Faculty of Animal Science, University of Agriculture in Krakow. Wool fibres were cleansed of grease and dirt using natural methods (water and natural soap). The water temperature did not exceed 40°C. After soaking, the samples were rinsed and dried on trays at room temperature. Sheep wool was a strengthening and modifying phase of the composite. Polylactic acid 2003D (NatureWorks, trade name Ingeo) was used as the matrix of the composite. The study was conducted at the laboratories of the Department of Biomaterials and Composites, Faculty of Materials Science and Ceramics, University of Science and Technology in Krakow.

Methods of producing the composite using sheep wool

White and black wool from Polish Mountain Sheep was used to prepare the composite material. To determine the effect of the presence of wool in the polylactide (PLA) matrix, composites with different contents of the wool fibre modifier were made.

The wool composite was made using an injection moulding method and a thermoforming method. We designed one control sample containing polylactide alone (G0 – 4 g of PLA) and eight experimental samples of the composite containing sheep wool (G1 – 4 g PLA + 0,1 g of black wool + 0,1 g of white wool, G2 – 4 g PLA + 0,2 g of white wool, G3 – 4 g PLA + 0,2 g of black wool,

G4 – 4 g PLA + 0,2 g of black wool + 0,2 g of white wool, G5 – 4 g PLA + 0,8 g of white wool, G6 – 4 g PLA + 0,8 g of black wool, G7 – 4 g PLA + 1,2 g of white wool, G8 – 4 g PLA + 1,2 g of black wool). The samples were obtained by the injection moulding method. Additionally, a 50x50 mm biocomposite box was made with wool fibre content of 85% ± 4%.

An injection moulder (Zamak Mercator, Poland) was used to make the composite by the injection moulding method. The injection moulding temperature was set at 225°C to prevent the polylactide and wool from degradation. The injection moulding process was performed as soon as possible after melting and homogenization of PLA and wool (homogenization in the extruder) to avoid degradation of the wool fibre (2 min melting and plasticization of PLA matrix, 10 sec injection moulding at a pressure of 10,000 N). The next stage of making the insulating plate from natural and biodegradable components was the production of the packaging film. The polylactide foil was made using a four-zone single-screw extruder (Zamak Mercator, Poland), which was filled with polylactide granules. The temperatures in zones 1, 2, 3 and 4 were set at 173°C, 169°C, 170°C and 170°C, respectively. The temperature in the joint between head and die was 170°C, and the head temperature was 170°C. The extrusion process produced thin films that were subsequently cut into pieces of about 16 cm. Next, the laminate was bonded with polylactide film. The polylactide film was placed on the prepared wool layer, and then the two layers were bonded using a temperature of 218°C until they were completely joined.

The composite laminate was made by high-temperature uniaxial thermoforming using a hydraulic press (Werther, Germany).

Analysis of the composite made by injection moulding

The composite samples obtained by injection moulding were examined under a Keyence VHX-900F digital microscope (Belgium). The surface wettability and wetting angle (contact angle) of the samples were determined with a Krüss DSA 10Mk2 goniometer (Germany). Ten measurements were made for each sample. The results were used to calculate the average wetting angle for each sample. The surface roughness of the materials and the Ra, Rt and Rz parameters were measured with a Hommel Tester T1000 profile meter using a TH300 sensor and a filter according to ISO 11562; the measuring range was 320 μm, the measuring length was 4,80 μm, and the sampling length was 0,8 mm. Infrared spectroscopy analysis was carried out on a Bruker Tensor 27 spectrometer. The analysis used the attenuated total reflectance (ATR) technique with a diamond crystal in the middle infrared range of 4000-600 cm^{-1}, with a 4 cm^{-1} resolution and 64 scans.

To evaluate the biodegradability of the composites, four selected samples (G 2, 3, 4, and 5) were analysed. The samples were placed in a beaker in soil sampled in Krakow and the beakers were placed in an ageing chamber with two ultraviolet lamps with an intensity of 35 W/cm^2 for 48 h. Then the samples were taken from the soil and washed with distilled water. One hour in the ageing chamber approximates 5,645 hours of exposure to natural solar radiation, and thus 48 h was equivalent to 30 years. Biodegraded samples were observed by microscopy (Keyence VHX-900F) to assess changes that had occurred in the composites. Observations were made of samples exposed to biodegradation in the soil as well as to those subjected only to ageing under UV radiation.

Analyses of the composite made by the thermoforming (hot pressing) method

The thermoformed composite (box) was subjected to thermal insulation tests. The hot-pressed composite (50x50 mm in size and with a wool fibre content of 85% ± 4%) was tested for thermal insulation over 20 h. An expanded polystyrene container commonly used for transporting

medicines was used as control packaging. Samples with water frozen at -80°C were placed in the experimental packaging (wool composite) and the control packaging, and the temperature was measured for 20 h.

RESULTS AND DISCUSSION

Analysis of the results for wetting angle in the samples obtained by injection moulding showed that the addition of wool increased the wetting angle (Table 1). The wetting angle for the control sample G0 was lowest at 54,4°. The highest wetting angle was obtained for the samples G4 (97,1°) and G1 (85,7°). Among the samples with added wool, the lowest wetting angle value was recorded for sample G5 (79,0°) (Table 1).

Table 1

Results of contact angle test for samples obtained by the injection method

Sample name	Type of sample	Contact angle [°]
G0 - control	4 g PLA	54,4
G1	4 g PLA + 0,1 g white wool + 0,1 g black wool	8,7
G2	4 g PLA + 0,2 g white wool	8,8
G3	4 g PLA + 0,2 g black wool	84,2
G4	4 g PLA + 0,2 g white wool + 0,2 g black wool	97,1
G5	4 g PLA + 0,8 g white wool	79,0
G6	4 g PLA + 0,8 g black wool	83,4
G7	4 g PLA + 1,2 g white wool	80,7
G8	4 g PLA + 1,2 g black wool	82,4

Surface roughness tests were performed for each sample based on three measurements, each of which covered a different measuring length. This yielded the average Ra, Rt and Rz values for the entire composite. The results showed that surface roughness increased considerably with the wool content of the samples (Table 2).

Table 2

Roughness results of samples produced by the injection method

Sample name	Wool/PLA weight ratio	Ra [µm]	Rt [µm]	Rz [µm]	$Ra_{śr}$ [µm]	σRa [µm]	$Rt_{śr}$ [µm]	σRt [µm]	$Rz_{śr}$ [µm]	σRz [µm]
		0,13	2,28	0,91						
G0	0,00	0,77	7,50	4,26	0,41	0,33	4,06	2,98	2,13	1,85
		0,33	2,39	1,21						
		0,29	11,56	3,16						
G1	0,05	0,81	19,08	7,79	0,91	0,68	16,48	4,26	7,03	3,55
		1,63	18,79	10,14						
		1,04	16,53	8,09						
G2	0,05	0,95	11,89	6,64	0,96	0,07	12,22	4,16	6,72	1,33
		0,90	8,23	5,43						
		0,13	1,11	0,68						
G3	0,05	0,18	3,32	1,65	0,57	0,72	7,23	8,76	3,72	4,46
		1,40	17,27	8,84						
		0,98	9,77	6,73						
G4	0,1	1,04	13,47	7,38	0,98	0,06	11,84	1,89	7,39	0,67
		0,93	12,29	8,06						
		0,82	13,07	7,75						
G5	0,2	0,48	12,74	5,49	1,30	1,14	20,45	13,06	12,16	9,66
		2,61	35,53	23,24						
		1,42	16,52	9,62						
G6	0,2	1,51	17,00	7,83	1,77	0,54	18,28	2,64	11,09	4,20
		2,39	21,32	15,83						
		1,58	22,16	12,14						
G7	0,3	1,10	17,37	8,20	1,47	0,33	17,63	4,41	10,29	1,98
		1,73	13,36	10,53						
		2,62	21,36	16,00						
G8	0,3	1,00	20,36	10,49	1,96	0,85	20,46	0,85	13,70	2,87
		2,26	19,66	14,62						

FTIR-ATR spectroscopy showed peaks at the same locations for the wool fibre samples and pure polylactide samples. This means that no new chemical bonds were formed in the material. FTIR spectra revealed no functional groups derived from wool fibre proteins, which demonstrates

good coverage of the fibres by the polylactide (PLA) matrices. The presence of hydroxyl groups on the fibres allows for good dispersion of fibres within the PLA matrix and prevents the agglomeration of fibres (Figures 1a and 1b).

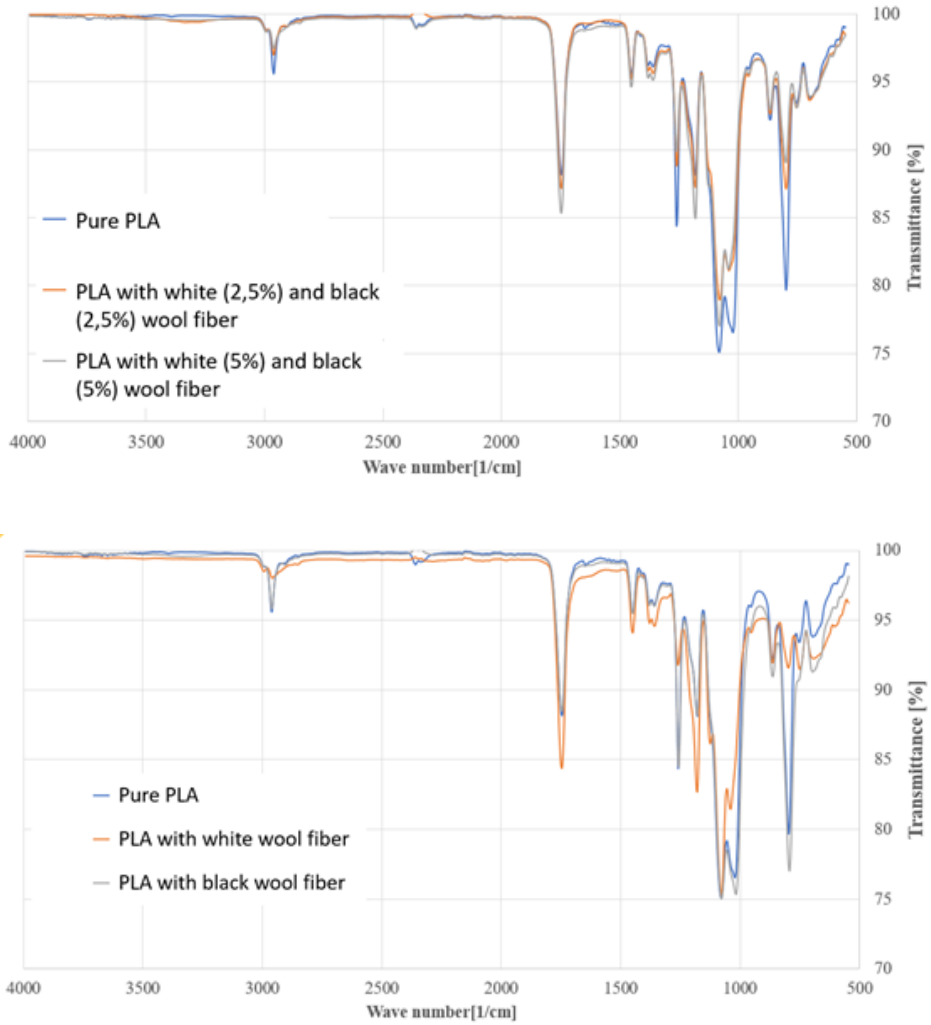

Fig. 1a and 1b. IR spectrum for pure PLA and composite wool/PLA samples

Real model tests of thermal insulating power demonstrated that the packaging with sheep wool fibre is effective at inhibiting temperature increase inside the packaging. The temperature measurements recorded over 21 h revealed that the composite packaging has similar thermal insulation characteristics to those of expanded polystyrene packaging (Figure 2).

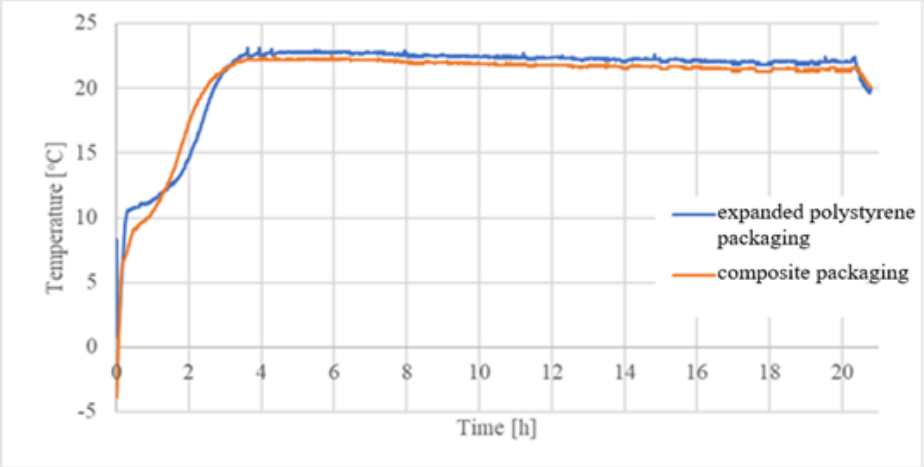

Fig. 2. Results of the thermal insulation test

Microscopic analyses of the samples before the ageing process showed that the fibres in the samples obtained by injection moulding were arranged randomly. Importantly, in the samples with high fibre content, the fibres were arranged in the direction of the injection moulding. The surface of the samples was smooth and showed no defects, and the fibres were evenly distributed. The addition of wool fibres accelerated the biodegradation process. Due to its hygroscopic properties, the wool transported water to the composted sample and hydrolysed (broke down) the sample from inside, as shown in microscopic photographs (Phot. 1).

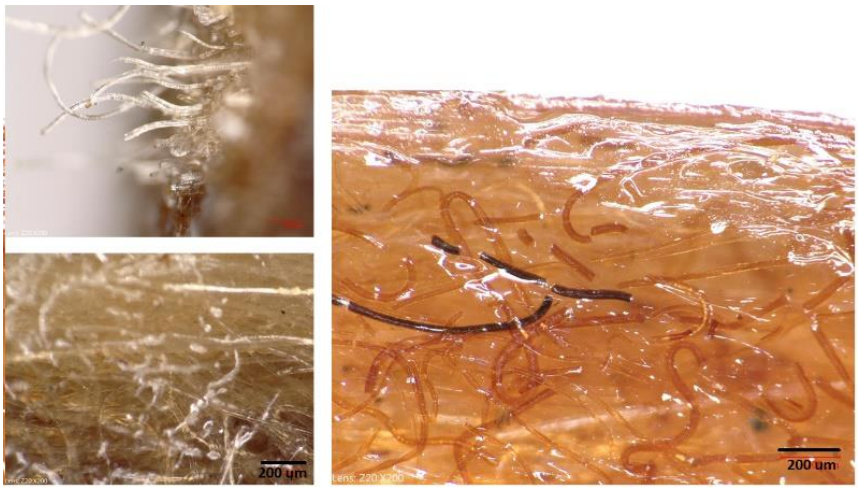

Photo 1. A microscope photo of a sample containing 0,8 g (4,8 g sample weight) of wool (G6) before the ageing process

Microscopic observations after the ageing process revealed that the pure polylactide samples and the composite samples with low wool content did not differ significantly in terms of biodegradability. However, accelerated biodegradability was found for the samples with high wool content (samples G7 and G8). This provides evidence that increased wool content accelerates this process considerably (Phot. 2 and 3).

Photo 2. Advancement of the biodegradation process in wool/PLA sample subjected to 48-h ageing in the ageing chamber (left G7, right G8)

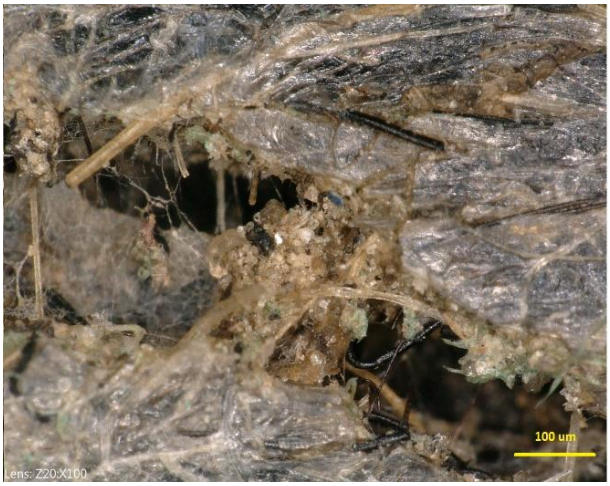

Photo 3. Advancement of the biodegradation process in wool/PLA sample (G8)

The present study showed that the addition of wool generally increased the wetting angle. This provides evidence that the addition of wool makes the composite less wettable, which means that it will provide better protection against moisture compared to pure polylactide. The laminates used have very similar wetting angles, so the addition of wool fibre may influence the physical properties of the surface irrespective of the testing technique (Andrzejewska and Topolinski, 2015). The results showed that surface roughness increased significantly with the wool content. This parameter describes the degree to which the surface of the biocomposites is uneven and how it is affected by wool. According to literature data, the higher the roughness, the quicker the breakdown of the packaging (Kaczmar and Pach, 2006). A rough surface and deep open porosity on the surface is conducive to the attachment of fungi and microorganisms involved in biodegradation (Phot. 4).

Photo 4. Photos of the PLA/sheep wool composite: left – freshly produced; middle – after composting in moist soil; right – after exposure to UV light

The material roughness index affects the rate of biodegradation of the composite. The greater the surface development, the more microorganisms will have access to the surface of the composted material (Chandramohan and Marimuthu, 2011; Akcagun et al., 2017).

For the wool fibre composites, peaks were observed to be at the same locations as for pure polylactide samples. This means that no new chemical bonds are formed in the material, as any new bonds would be recorded as separate peaks in the spectrum. Owing to the presence of hydroxyl groups in wool fibre, the PLA mixture is easily homogenized in processing technology (Qin et al.,

2011). This is an important feature for the use of this biocomposite in industry, building engineering, and agriculture (Azwa et al., 2013; Kim et al., 2015).

The tests for thermal insulating power (results in Fig. 2) demonstrated that the composite packaging containing wool fibre had the same characteristics as the expanded polystyrene packaging. The introduction of the wool felt modifier, which shows thermal insulation properties, into the PLA matrix improved the thermal insulation of the designed and tested biocomposite as a whole. Sheep wool and felt made from it have good thermal insulation properties (Mao and Russel, 2007; Mukherjee and Kao, 2011; Gieremek and Cieśla, 2012). Therefore, the use of this fibre resulted in a composite with good thermal insulation properties. Thermal insulation and biodegradability are important aspects of the composite. Microscopic observations revealed little difference in the biodegradability of the pure polylactide samples and low-wool samples, whereas the samples with high wool were biodegraded. This indicates that increased wool content considerably accelerates this process. Today, due to packaging waste management problems, much packaging waste does not enter the waste neutralization system (Latos-Brozio and Masek, 2020; Ragaišienė et al., 2016). The composite produced and tested in the present study will decompose completely without harming the environment, even if it does not reach the waste management system. Composite materials with natural phases (wool fibre/biodegradable matrix) are not subject to waste law and can be decomposed in compost bins, and when they reach a landfill they will be reduced with time to H_2O and CO_2 (Bledzki and Gassan, 1999; Getme and Patel, 2020).

CONCLUSION

Wool fibre, which has unique physicochemical characteristics, can be used as a component of composite materials, in line with the strategy of bioeconomy and sustainable development. The search for alternative solutions for mixed wool management may support sheep farming in Poland. The present study involving sheep wool demonstrated that the hydrophobicity of a material increases with the wool fibre content of the samples. The packaging containing sheep wool fibre has good insulating properties and is biodegradable. The development of a composite technology involving sheep wool for use in the construction industry, agriculture or medicine may help to put this type of fibre to use in Poland. Furthermore, our study showed that the composite product is biodegradable and may offer an alternative to the commonly used expanded polystyrene packaging. The introduction of sheep wool fibre-reinforced composites will contribute to the economic activation of mountain regions and have a positive environmental impact.

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