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Comparison of Selected Chemical Properties of Fibres from Different Breeds of Dogs and German Blackface Sheep

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Abstract
Combed or picked out dog hair fibre, as one of the protein fibres, could be used in yarn manufacturing. Dog hair fibres have a specific scale structure, shape and distribution on the surface. Results obtained indicated that same dog hair fibre fragmented and interrupted the continuous whole and continuous kemp medulla inside. Thus it is necessary to find differences between sheep wool and dog hair fibres as well as between different dog breeds in other areas. In this research, the crystal and chemical structures, macro-chain confirmation and surface morphology of sheep wool and dog hair fibres from different breeds were investigated through identifying variations between thus protein fibres. FTIR analysis showed that the absorbing peaks of sheep's wool around 2920 cm^{-1} and 2850 cm^{-1} are more intense and sharper than those in the IR spectrum of dog hair fibre. Other peaks of the dog hair spectra are more intensive and have a bigger areal. Values of the crystallinity degree and indexes are different not only between sheep wool and dog hair fibres, but also among hairs of the different dog breeds too. The percentage amounts of carbon, hydrogen and nitrogen in sheep wool and dog hair fibres are of the same order of magnitude. However, the content of elements in the cortex of sheep wool and dog hair fibres varies, especially that of sulphur and oxygen, which varies by about two times among the different protein fibres.

Key words: *dog hair fibre, chemical structure, surface morphology, elemental analysis, crystallinity.*

Introduction

The combined physicochemical and structural investigations [1] indicate the great inhomogeneity of the material of wool fibres. Wool is a complex multicell system composed of inanimate cells which differ in composition, shape and properties. It is well known that keratin is a major structural fibrous protein providing an outer covering, such as hair, wool, feathers, nails and horns of mammals, reptiles and birds [2]. Hydrothermal, acid, alkaline, and enzymatic hydrolysis are the main methods of keratin extraction [3].Wool is defined as a protein fibre which has very exclusive properties: natural crimp, surface structure, cross-section, and even chemical consistency [4 – 6]. Hair fibres tend to have low mechanical properties compared to plant fibres. However, they tend to have excellent thermal properties. The scales on the surface of wool fibre provide warmth, good moisture adsorption and make wool fibre very popular in the textile industry [7 – 9].

In literature there is not so much information about dog fibre and the possibilities of blending it with other fibre, i. e. wool, cotton and linen. But combed or picked out dog hair fibre, as one of the protein fibres, could be blended with others and used in yarn manufacturing [10, 11]. Previous studies [12] have shown that investigated dog hair fibres (Chow Chow, Pekingese and Yorkshire terrier) have more crimp and a smoother surface than sheep wool fibre (a primitive Lithuanian breed); also dog hair fibres have an irregular round shaped medulla inside the hair. Moreover it was established that the geometrical properties of the fibres influence their mechanical properties [12]. It is known that those of the fibres and the diameter of the medulla depend on many factors: nutrition, animal age, animal body region, the stage of hair growth, the time of cutting the hair, nutrition and the grazing place.

Hence wool fibre is a very complicated subject of research. The complexity of wool fibre may affect not only the variety of results of geometrical and mechanical indices, but even the factors influencing these results. The best proof for this is the fact that in spite of many studies made over the last 70 years, the problem of the structure of this system has not yet been fully resolved. Wool is composed of a cuticle and cortex, and a medulla only in the case of course wool. The cuticle has valine, disulfide bond groups and carboxyl groups, whereas the cortex makes up the main portion of the wool. It is composed of more than 18 amino acids, which can be divided into four distinct groups: cationic, anionic, nonpolar,

and polar. The main functional groups include carboxyl (–COOH), amino ($–NH_2$), and hydroxyl (–OH) groups; thus the chemical properties are extremely active [7, 13].

Infrared absorption spectroscopy is one of the methods used in the analysis and estimation of changes in the wool structure. The spectra of wool fibre keratin indicate characteristic absorption bands assigned mainly to the peptide bond (–CONH–), which represents the fundamental structural unit of the polypeptide chain. It was found that the (C–N) bond in this arrangement partially has the nature of a double bond and all four atoms of the peptide bond are situated on one plane which can twist around (C–C) and (N–C) bonds. This twisting differs depending on the adjacent amino acids. These interactions define the secondary structure of the polypeptide chain in a given place [13].

The purpose of this research was to investigate the crystal and chemical structures, macro-chain confirmation and surface morphology of protein fibres and to identify differences between German Blackface sheep wool and different breeds' dog hair fibres, as well as between dog fibres too.

Wide-angle X-ray diffraction (WAXD), Fourier transform infrared spectrometry (FT-IR), Scanning electron microscopy (SEM) and elemental analysis of Carbon, Hydrogen & Nitrogen (CHN) were used in this research

Materials and methods

Several protein fibres (sheep wool and dogs hair) were investigated in this research. These fibres were indicated as: 1 – German Blackface sheep, 2 – Yorkshire Terrier, 3 – Flemish Bubje, 4 – Poodle, 5 – Shih-Tzu, 6 – Bobteil, 7 – Russian Spaniel, 8 – English Spaniel, 9 – American Spaniel. German Blackface sheep wool was taken from a sheep farm from the Anykščiai district, Lithuania. Dog hair fibres were collected from dog hairdressing salons (2, 4, 5, 7 - 9), a breeding-ground of dogs (6) and private dog breeders (3) in Lithuania. Hairs were cut from different part of the animal's body. All fibres were not laundered or chemically affected.

The mean fibre diameter (MFD) was measured by a Sirolan Laserscan, with results reported in micrometers (μm) [14]. The device was turned on and left for two hours for stabilisation of all parameters, as specified in the standard (IWTO-12-95). The samples of length (l = 2 mm) of every fibre were made using a guillotine. Two thousand fibres were measured in one test and 8 tests were made for every type of fibre. Also the coefficient of variation of the fibre diameter was calculated.

IR spectroscopy

An infrared spectrum was obtained using a Perkin-Elmer FTIR Spectrum GX (USA) spectrometer. The resolution was 1 cm^{-1}, scan rate 0.2 $cm \cdot s^{-1}$ and scan number 16 times. "Spectrum 5.0.1" software was used for calculation of the area of the peaks in the spectra ΔS in $A \cdot cm^{-1}$. Samples for IR spectroscopic analyses were prepared as pellets using 200 mg of optically pure KBr and 2 mg of cut fibres. The protein fibres were cut in short, 1 - 2 mm length segments. After that, samples 10 mm in diameter and 0.5 mm in thickness were made and put in a special holder. Characteristic spectra of the pellets prepared were scanned in the wave number range of 4000 cm^{-1} – 500 cm^{-1}.

X-ray diffraction analysis of protein fibres

A wide-angle X-ray diffraction (WAXD) analysis of sheep's wool and dog hair samples at different was performed on a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) operating at a tube voltage of 40 kV and tube current of 40 mA. Dry felted fibres were mounted on a sample holder for X-ray diffraction analysis. The X-ray beam was filtered with a Ni 0.02 mm filter to select the CuKα wavelength. Wide-angle diffraction patterns were recorded in Bragg-Brentano geometry using a fast counting detector - Bruker LynxEye based on silicon strip technology. The specimens were scanned over the range 2θ = 3 – 45° in a scanning step of 0.02° and at a scanning speed of 6° min^{-1} using a coupled two theta/theta scan type. In this study a crystallinity index was defined by the method described previously [15, 16] and calculated according to ***Equation 1***.

$$C_r \cdot I = \frac{I_{9^\circ} - I_{14^\circ}}{I_{9^\circ}} \times 100\% \qquad (1)$$

where, $C_r \cdot I$ is the crystallinity index, referring to the relative crystallinity degree of wool hair, I_{9° the maximum intensity (in arbitrary units, also as . u.) of crystal lattice diffraction with 2Θ at about 9°, and I_{14° is the minimum diffraction intensity in the same unit with 2Θ at about 14°.

Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM/EDS)

SEM imaging was performed using a Scanning Electron Microscope (SEM) Quanta 200 FEG (FEI, the Netherlands) operating in the variable pressure mode, magnification – 5000×, scale – 20 and magnification – 2000×, 50 μm. Samples of protein fibres were imaged under a residual pressure of 80 Pa, sufficient to avoid imaging artefacts, e.g. sample charging, commonly resulting during high energy electron beam analysis. Energy dispersive spectroscopy (EDS) was performed using a Bruker XFlash 4030 detector. A sample cros-section was prepared by cutting fibre with liquid nitrogen and mounted for imaging using carbon tape.

Other methods

Elemental analyses of sheep wool and dog hair fibres were performed on a dry (moisture-free) basis using a model Elemental Analyzer CE-440 (Control Equipment Corporation, USA). The nitrogen, carbon, and hydrogen contents were determined directly and their results were found to be in good agreement (± 0.2%) with the values calculated.

Results and discussions

Diameter is a very important property of all natural fibres, especially protein fibres. There are several methods for the measurement of wool mean fibre diameter: an optical fibre diameter analyser (OFDA), single fibre analyser (SIFAN), computer images analysis, Sirolan Laserscan etc. Laserscan offers all the advantages of airflow, as well as the additional advantage of even more information about wool fibre characteristics such as distribution in the diameter, comfort factors and curvature [17]. In this research the Sirolan Laserscan method was used because of the big number of measurements in a short time (16000 for every fibre) and automatically calculated statistical data of the mean fibre diameter investigated.

Table 1. *Mean fibre diameter of sheep wool and dog hair fibre.*

Fibre symbol	1	2	3	4	5	6	7	8	9
X, μm	31.8 ± 0.73	27.2 ± 0.78	36.6 ± 0.79	22.1 ± 0.43	29.6 ± 0.90	48.8 ± 2.73	24.9 ± 0.44	25.0 ± 0.20	23.7 ± 0.33
V, %	25.5	27.7	25.2	27.6	31.9	28.3	25.7	26.4	33.3

Table 1 presents calculated values (estimated using Sirolan Laserscan equipment) of MFD i.e. average value (χ), coefficient of variation (V) and the absolute random error (Δ). It was estimated that the mean fibre diameter (MFD) of the fibres investigated varies in the range of 22.1 – 48.8 μm and coefficient of variation of the fibres investigated from 25.2 to 33.3%.

It is known that the outer layer of common animal fibre is covered by scales, and the scale structure pattern can be described by many absolute parameters, such as the scale frequency and scale edge size among others. The scale structure pattern of some fibres investigated are presented in ***Figure 1***.

It can be seen from the photographs that the scale frequency, height and edge size are different. Dog hair fibres have a specific scale structure which differs from sheep wool fibre: scales are smaller, and the scale shape and distribution are more located on the surface. Moreover our earlier investigation [12] shows that some protein fibres have different types and size medullas inside them. In this study were obtained results where all fibres investigated have medulla inside the hairs, except Flemish Bubje dog hair and German Blackface sheep wool fibres. Some of the SEM images of the fibres investigated are presented in ***Figure 2***.

Photographs show that protein fibres have an irregular round form cross-section, round form structure and a whole or spongy structure medulla is located in the centre or near the centre of fibres. Also it was established that the population of medulla varies in the range of 6.6 - 61.54%, and the medulla can be fragmented, interrupted, continuous and continuous kemp. Results Obtained showed that Bobteil breed and Shih-Tzu breed dog hair fibre have a whole or spongy structure of medulla. Moreover English Spaniel and Poodle breed dog fibres have a porous medulla, while Yorkshire Terrier and Russian Spaniel dog fibres have a hollow type medulla inside the hair. The scale frequency of dog hair fibres is higher than for sheep's wool, whereas values of the scale height of sheep's wool are higher than for dog hair fibre. These differences may help to identify the kind of protein fibre in the blend.

It can be concluded that a comparable analysis of the structural properties, cross-section and diameter of sheep's wool and dog hair fibres of the eight breeds show that these fibres are very different. Thus in the next stage of this research these protein fibres will be compared through investigating their crystal and chemical structures, macro-chain conformation and surface morphology.

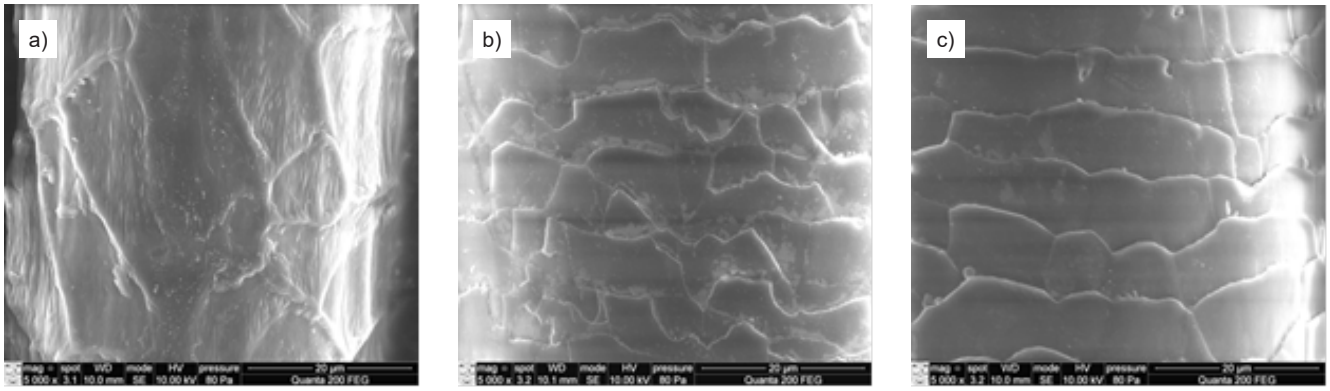

Figure 1. *SEM images of German Blackface sheep wool, Yorkshire Terrier and Russian Spaniel fibres. (Magnification – 5000×, scale – 20 μm). a) 1 – German Blackface sheep, b) 2 – Yorkshire Terrier, c) 7 – Russian Spaniel.*

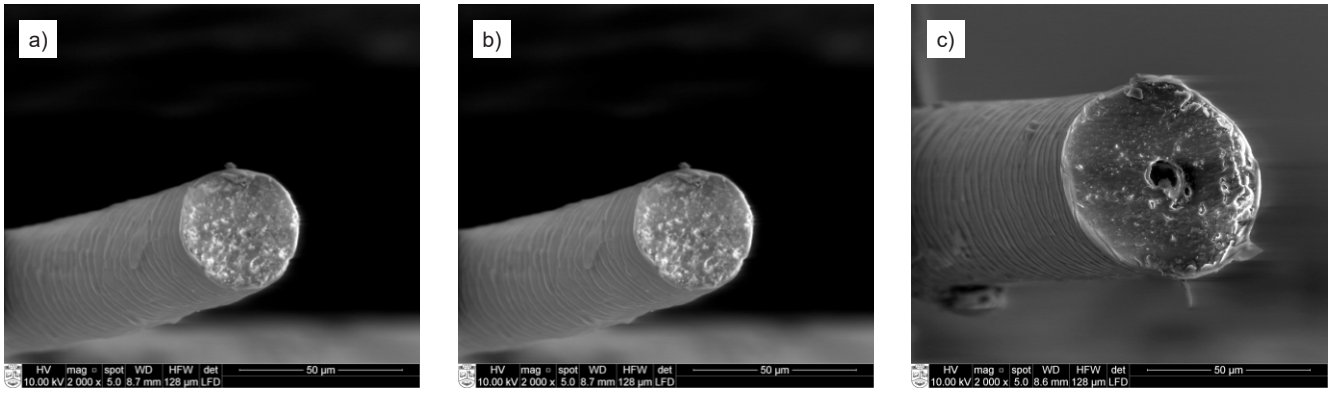

Figure 2. *SEM images of Russian Spaniel, American Spaniel and Shih-Tzu dog hair fibres, (Magnification – 2000×, scale – 50 μm). a) 7 – Russian Spaniel, b) 9 - American Spaniel, c) 5 - Shih-Tzu.*

Table 2. *EDS analysis of the cortex of sheep wool fibre and dog hair fibres of different breeds.*

Protein fibre	Content of elements, %			
	Carbon	Nitrogen	Oxygen	Sulfur
1. German Blackface sheep	66.2	14.8	18.0	1.0
2. Yorkshire Terrier	58.7	17.2	21.9	2.2
3. Flemish Bubje	43.7	17.9	36.1	2.3
4. Poodle	43.3	18.8	35.6	2.4
5. Shih–Tzu	43.4	18.4	35.6	2.6
6. Bobteil	41.6	19.4	36.5	2.5
7. Russian Spaniel	42.6	18.2	36.8	2.5
8. English Spaniel	44.5	16.6	36.5	2.4
9. American Spaniel	44.0	17.7	36.0	2.3

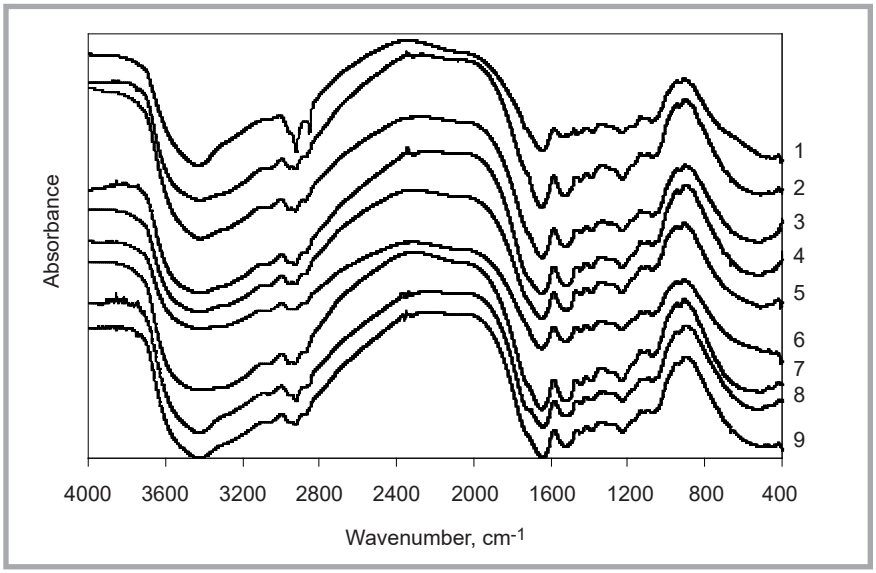

Figure 3. *IR spectra of protein fibres: 1 – German Blackface sheep, 2 – Yorkshire Terrier, 3 – Flemish Bubje, 4 – Poodle, 5 – Shih –Tzu, 6 – Bobteil, 7 – Russian Spaniel, 8 – English Spaniel, 9 – American Spaniel.*

Firstly EDS analysis of the cortex of protein fibres was done. The content of basic chemical elements: carbon, nitrogen, oxygen and sulphur (C, N, O, S) in the cortex of the fibres investigated is presented in ***Table 2***.

Data presented in the ***Table 2*** show that the content of basic chemical elements (C, N, O, S) in the cortex of sheep wool and dog hair fibres was different in this research. The concentration of sulphur, oxygen and nitrogen in sheep wool was lower than in dog hair: the content of sulphur and oxygen was lower by two times (except Yorkshire Terrier), and the content of nitrogen by 1.12 - 1.31 times. The content of carbon in dog hair fibres varied in the range of 41.6 - 58.7% and the highest amount (66.2%) of this chemical element was observed in the cortex of German blackface sheep wool. It was found that the elemental composition of the cortex among almost all dog hair fibres measured was comparable, with only the contents of carbon (58.7%) and oxygen (21.9%) in Yorkshire Terrier hair fibres being different.

To obtain additional information about possible differences between sheep wool and dogs hair fibre, analysis of the IR spectra of these wool hair samples was attempted. Sheep wool and eight dog wool hair spectra are plotted simultaneously. It allows great precision in the spectra infrared light absorption intensity (see ***Figure 3***).

It can be seen in ***Figure 3*** that the spectra are very similar and their analysis did not highlight any unusual peaks; but there is a different intensity of some peaks and their area. The spectrum of sheep's wool is chosen as the reading level.

Peaks in the range 3500 – 3200 cm^{-1} are attributed to N–H and O–H valence vibrations [18]. The peak's position of 3433 cm^{-1} moves slightly into the range of lower wavenumbers. A weak band which is an overtone of the amide II bands appears at 3100 –3060 cm^{-1}. Here the peak's position is at 3433 cm^{-1}. All peaks of dog hair fibre spectra are more intensive and have a bigger areal in both the ranges described (see ***Table 3.a***).

Various C–H bands are reflected by peaks in the range 3000 – 2800 cm^{-1} [19]. All spectra of dog hair fibre investigated have three peaks in this range (see ***Figure 4*** and ***Table 3.a***). The sheep wool spectrum has no visible peak at 2958 cm^{-1} , meanwhile in the case of dog wool spectrums the peak in the similar frequency zone is obvious. The other two peaks at 2920 and 2851 cm^{-1} shifted towards a shorter wavelength direction. These two peaks are of more intensity and their areal of band is bigger than those in the spectrums of dog hairs (see ***Figure 4*** and ***Table 3.a***). In the amide I region 1700 – 1600 cm^{-1} each type of secondary

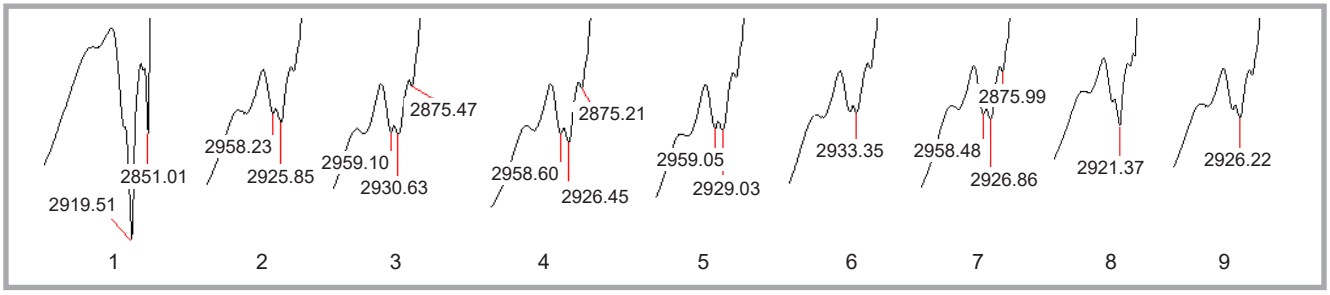

Figure 4. *Comparison of IR spectra of protein fibres in the range 3000–2800 cm^{-1}: 1 – German Blackface sheep, 2 – Yorkshire Terrier, 3 – Flemish Bubje, 4 – Poodle, 5 – Shih Tzu, 6 – Bobteil, 7 – Russian Spaniel, 8 – English Spaniel, 9 – American Spaniel.*

Table 3.a. *Data of IR spectrum quantitative analysis in wavenumber region of 3500 – 2800 cm^{-1}.*

Sample of protein fibre	Functional group or bond to which the vibration is attributed									
	N–H, O–H		Secondary amide, amide II overtone		Methylene symmetric C–H stretching		Methylene asymmetric C–H stretching		Methylene asymmetric C–H stretching	
	Band position	Area of band	Band position	Area of band	Band position	Area of band	Band position	Area of band	Band position	Area of band
German Blackface sheep	3433	142.8	3068	14.0	–	–	2920	23.4	2851	12.8
Yorkshire Terrier	3417	158.9	3068	19.1	2958	10.6	2925	12.6	2873	9.6
Flemish Bubje	3421	178.2	3067	26.1	2958	12.0	2929	13.2	2873	11.2
Poodle	3421	189.3	3068	28.0	2958	12.1	2926	13.3	2875	11.3
Shih Tzu	3423	170.4	3068	23.9	2958	10.7	2929	11.7	2873	9.7
Bobteil	3417	127.8	3067	18.5	2959	8.4	2928	9.9	2873	8.5
Russian Spaniel	3417	208.8	3068	30.3	2958	12.3	2930	16.3	2875	11.6
English Spaniel	3426	207.7	3063	28.9	2953	6.3	2919	14.8	2873	11.7
American Spaniel	3426	183.1	3067	25.7	2958	11.6	2924	12.8	2873	10.9

Table 3.b. *Data of IR spectrum quantitative analysis in wavenumber region of 1650–1500 cm^{-1}*

Sample of protein fibre	Functional group or bond to which the vibration is attributed											
	Amide I band (=C=O)		Secondary amide N–H bending, C–N wagging		Amide band (III)		(S=O) cysteic acid		(S=O) cysteic dioxide		(S=O) cysteic monoxide	
	Band position	Area of band	Band position	Area of band	Band position	Area of band	Band position	Area of band	Band position	Area of band	Band position	Area of band
German Blackface sheep	1643	26.2	1546	19.0	1235	17.6	1171	6.4	1125	6.0	1077	6.3
Yorkshire Terrier	1651	37.4	1537	27.8	1235	21.3	1171	7.4	1125	6.9	1077	7.3
Flemish Bubje	1648	49.8	1533	36.4	1235	44.9	1170	11.6	1126	9.9	1076	14.4
Poodle	1650	45.9	1514	32.5	1235	40.4	1171	10.0	1125	8.4	1076	9.5
Shih Tzu	1648	41.4	1526	30.4	1235	36.44	1171	9.1	1125	7.6	1077	8.6
Bobteil	1648	33.5	1527	25.3	1235	31.6	1170	8.1	1126	6.9	1077	7.8
Russian Spaniel	1649	53.4	1525	41.4	1235	48.5	1171	12.2	1125	10.2	1077	11.7
English Spaniel	1646	49.4	1518	36.0	1234	44.2	1172	11.3	1120	9.5	1076	13.7
American Spaniel	1646	45.2	1518	32.4	1234	39.9	1170	10.2	1126	8.7	1078	12.4

structure gives rise to a somewhat different C=O stretching frequency due to the unique molecular geometry and hydrogen bonding pattern [20]. Peak positions in different dog hair spectra, which can be attributed to the amide I band, vary slightly in the interval of 1651 – 1646 cm^{-1}. While the peak in the spectra of the sheep wool position is at 1643 cm^{-1} (see ***Table 3.b***). As reported in literature source [21], a component centred between approximately at 1658 and 1650 cm^{-1} was assigned to the α-helix, which is consistent with both the theoretical calculation and observation of bands in the spectra of α-helical proteins. The unordered conformation is usually associated with the band between 1640 and 1648 cm^{-1}.

The amide II band for secondary amides is due to the coupling of N–H bending and C–N stretching and appears at 1560 – 1530 cm^{-1} [19]. All spectra investigated have peaks in both the ranges described, and the peaks of dog wool spectra are more intensive and have a bigger areal. However, peaks attributed to amide II band have different positions (see ***Table 3.b***). All peak positions of different dog hair spectra, which can be attributed to the amide II band, vary in the interval of 1514 – 1537 cm^{-1} and shift towards the shorter wavelengths direction. All these peaks have more intensity and their areal of the band are bigger than those in the spectrum of sheep wool (see ***Figure 3*** and ***Table 3.b***). The position and intensity variability of amide bands is attributed to the change in conformation of the keratin molecule of wool. On the basis of literature data [13, 22] the separation of absorption maxims for amide I (1650 cm^{-1}) and amide II (1547 cm^{-1}) suggests the resence of an α-helix structure in the keratin chain, whereas the bands of amide I (1638 cm^{-1}) and amide II (1515 cm^{-1}) indicate the presence of a keratin secondary structure of the β-sheet type [23]. Hence according to data presented in the literature, it can be expected that Poodle, English and American Spaniel hair keratin are of two types – α-helix and β-sheet.

The amide III band occurs in the range of 1220–1300 cm^{-1} [13]. The peak position at 1235 cm^{-1} did not change but its intensity is higher than usual in the other range of wavelengths in spectrums of the dog hair.

The region of 1200 – 1000 cm^{-1} is associated with the vibrations of sulphur-oxygen groups of keratin [24]. There are three peaks in the spectrums of sheep's and dog's wool, with wave's numbers of 1171, 1125 and 1077 cm^{-1}. Well defined peaks at 1040 and 1173 cm^{-1} are assigned to S=O stretching vibration originating from cystic acid [8]. The trend of peak intensity change is the same as for peaks in the amide III band.

Summarising the IR spectroscopy results, as can be seen from ***Figure 4*** showing fragments of IR spectra for sheep wool and dog hair fibre used in the experiments presented earlier (***Figure 3,*** data from ***Table 3.a*** and ***3.b***), it can be said that the intensity and areal of peaks of sheep's wool with dog's wool showed obvious change in the range 3000 – 2800 cm^{-1} When in other regions of the IR spectrum the wave does not have such clear differences.

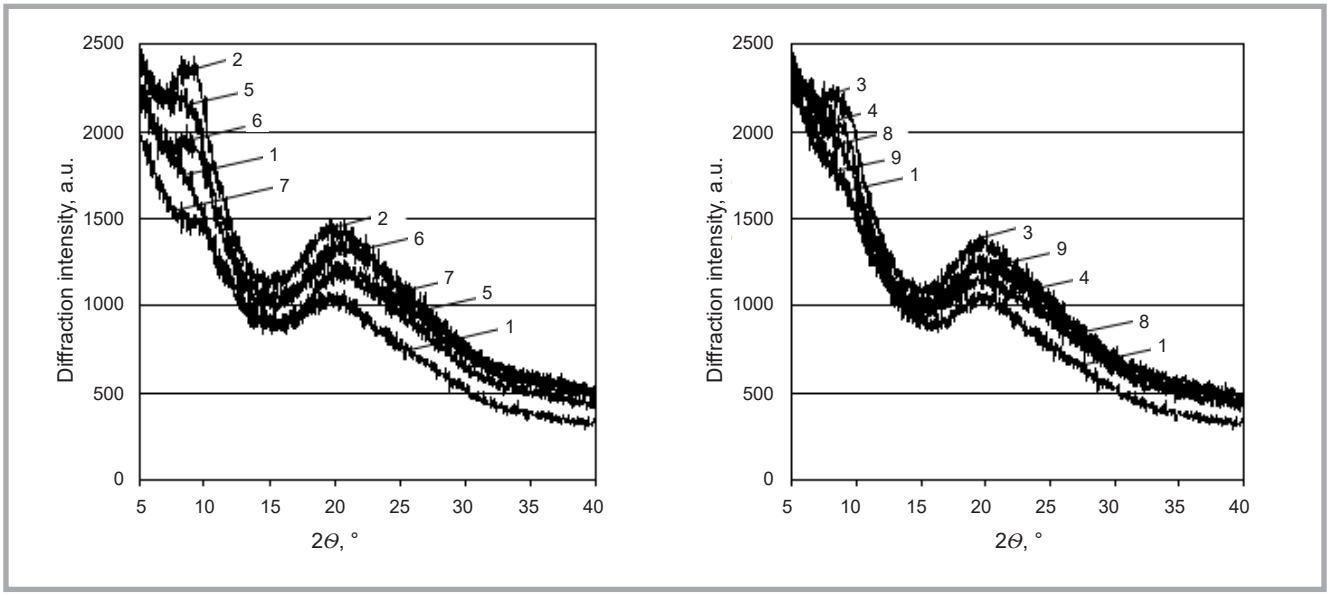

Figure 5. *XRD patterns of protein fibres: 1 – German Blackface sheep, 2 – Yorkshire Terrier, 3 – Russian Spaniel, 4 – Poodle, 5 – Shih Tzu, 6 – Bobteil, 7 – Flemish Bubje, 8 – English Spaniel, 9 – American Spaniel.*

The crystallinity of wool fibre plays an important role in its chemical, thermal, optical and other physical properties [25]. Wool fibre has a kind of macromolecular polymer structure between the crystal region and amorphous region [26]. According to known reports [27 – 30], there are three crystal diffraction peaks: the meridional reflections (Bragg angle 2Θ between 15° and 31°) for the α-helix structure, the equatorial reflections (Bragg angle 2Θ between 16° and 31°) for the β-sheet structure, and the equatorial reflections (Bragg angle 2Θ = 9°) for the α-helix and β-sheet structure of peptide chains in wool. Results of X-ray diffraction of the protein samples are shown in ***Figure 5***.

They show a typical diffraction pattern of keratin with a medium peak at Bragg angle 2Θ = 9.04 ~ 9.08° and prominent peak at 2Θ = 20.58 ~ 20.68°. Moreover a diffraction peak valley was observed at 2Θ = 13.78 ~ 13.88° between the two characteristic diffraction peaks mentioned above, which was assigned to the amorphous region of wool fibre. ***Figure 5*** also shows that the peak intensities of both characteristic peaks at 2Θ = 9.04 ~ 9.08° and 2Θ = 20.58 ~ 20.68° change depending on the protein fibre sample. The most intensive peaks of both characteristic peaks were established for Yorkshire Terrier dog fibre, while the least intensive peak of the characteristic peak at 2Θ = 9.04 ~ 9.08° was for Flemish Bubje dog and German Blackface sheep fibre. The least intensive peak of the characteristic peak at 2Θ = 20.58 ~ 20.68° was found for German Blackface sheep fibre as well. Mentioned peaks of other dog fibres investigated are located between the highest and lowest values. Thuse it was established that the peak intensities of the both characteristic peaks at 2Θ = 9.04 ~ 9.08° and 2Θ = 20.58 ~ 20.68° are different for dog and sheep fibres.

Table 4. *Crystallization indexes of sheep wool fibres and dog hair fibres of different breeds.*

Number of sample	Kind of wool	$I_{9.08°}$, a.u.	$I_{13.88°}$, a.u.	$C_r \cdot I$, %
1	German Blackface sheep	1769.186	916.335	48.21
2	Yorkshire Terrier	2348.444	1154.966	50.82
3	Flemish Bubje	1466.779	875.556	40.31
4	Poodle	2061.026	943.154	54.24
5	Shih Tzu	2156.566	1064.947	50.62
6	Bobteil	1997.962	1017.783	49.06
7	Russian Spaniel	2170.962	1081.087	50.20
8	English Spaniel	1917.702	1027.922	46.40
9	American Spaniel	1759.111	945.731	46.24

Table 5. *Elemental analysis of sheep wool fibres and dog hair fibres of different breeds.*

Protein fibre	Content of elements of weight, %			
	Carbon	Hydrogen	Nitrogen	Other
1. German Blackface sheep	47.14	6.29	15.14	31.43
2. Yorkshire Terrier	42.38	6.19	13.84	37.60
3. Flemish Bubje	45.05	6.05	14.89	34.01
4. Poodle	45.20	5.69	14.69	34.42
5. Shih –Tzu	48.04	6.32	15.64	30.00
6. Bobteil	44.91	6.24	15.00	33.86
7. Russian Spaniel	43.84	5.93	14.44	35.79
8. English Spaniel	47.60	6.11	15.41	30.88
9. American Spaniel	45.29	5.80	14.73	34.17

It was established that the crystallinity of the protein fibres investigated are different, varying in the range of 40.31 – 54.24% (***Table 4***).

It can be seen from ***Table 4*** that the crystallinity degree of different breeds' dog hair fibres is more diverse comparing with German blackface sheep wool fibre. For example, the maximal value of the crystallinity index (54.24%) was measured for dog hair fibre of the Poodle breed, and the minimum (40.31%) for Flemish Bubje. Probably

these results could be explained by the structure of fibres. The diameter of Poodle dog fibre is the lowest of all fibres investigated, and the diameter of Flemish Bubje dog fibre is the one of the highest (see ***Table 1***). Moreover it was found that Flemish Bubje fibre does not have a medulla inside, while Poodle dog fibre has.

To better understand differences between the several protein fibres, the chemical composition of sheep wool and dog hair fibre was investigated and the percentage amounts of carbon, hydrogen and nitrogen was measured in this study (see ***Table 5***).

As shown in ***Table 5***, the percentage amounts of the above-mentioned chemical elements (carbon, hydrogen and nitrogen) in sheep wool and dog hair fibres are of the same order of magnitude, and results slightly varied in the range of C ~ 45 ± 3.0%, H ~ 6 ± 0.3% and N ~ 14.6 ± 1.0%, respectively. Therefore this variation is 0.067% for carbon, 0.05% for hydrogen and 0.068% for nitrogen among all fibres measured. Overall the percentage amount of C, H and N in almost all dog hair fibres was found to be decreased compared with sheep's wool. Only the percentage composition of Shih-Tzu (C:H:N 48.04:6.32:15.64) and English Spaniel (C:H:N 47.6:6.11:15.41) dog hair fibres is similar to German blackface (C:H:N 47.14:6.29:15.14) sheep wool.

The results obtained from this research are difficult to interpret unequivocally, because there is not much comparable information from other scientists' papers. As is seen from data presented in ***Tables 2*** and ***5***, the elemental composition determined in different ways is dissimilar. As was expected, the values of carbon and nitrogen chemical elements (C, N) in the cortex of fibre is slightly differ from those of these elements determined on a dry basis using an Elemental Analyzer CE-440. For example, values of nitrogen in the cortex vary from 14.8% to 19.4% for all fibres investigated, being determined on a dry basis in the range of 13.8 – 15.6%. Hence the differences in some kinds of fibre (Yorkshire Terrier, Poodle, Bobteil and Russian Spaniel) are about 20%, while values of nitrogen of German Blackface sheep and English Spaniel fibre differ only by 2.3 – 7.2%. The biggest difference between carbon values (28.8%), determined in the cortex and on a dry basic was established for German Blackface sheep fibre. For better comparison and understanding of peculiarities of the protein fibres' chemical structure, it was decided to include wool from other breeds of sheep in our future investigations.

Conclusions

It is possible to make woollen yarns from sheep wool and dog hair fibres to knit scarves, gloves, hats, a heating neck or spine belt, as well as to make felts from these fibres to protect people from the cold or rheumatic diseases. After cutting dog hair fibres, they usually are discarded and not used in any further appliance at this moment. Hence this could be a useful and purposeful exploitation of an unused resource.

Comparative analysis of the structural properties and cross-section of sheep's wool and dog hair fibres of eight breeds shows that these fibres visually are very different, with their diameter varying from 22.1 to 48.8 μm.

FTIR analysis showed that there was no change in the composition of chemical groups in the macromolecular of German blackface sheep wool and different dog hair fibres; but a different intensity of some peaks and their area were found. The absorbing peaks of sheep's wool around 2920 and 2850 cm^{-1} are more intense and sharper than those in the IR spectre of dog hair fibre. Other peaks of the dogs hair spectra are more intensive and have a bigger areal.

It was measured that values of crystallinity degree and indexes are different not only between sheep wool and dog hair fibres, but also among hair of the different dog breeds as well. The crystallinity index of these fibres varies from 40.31% (Flemish Bubje dog fibre) to 54.24% (Poodle dog fibre).

The percentage amounts of carbon, hydrogen and nitrogen in sheep wool and dog hair fibres are of the same order of magnitude. However, the content of elements in the cortex of sheep wool and dog hair fibres vary, especially the contents of sulphur and oxygen, which vary by about two times among the different protein fibres.

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