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Fibrous Composites Based on Keratin from Chicken Feathers

Abstract
A new unique technology is presented, developed for manufacturing fibrous composites based on keratin from chicken feathers, with a content up to 70%. The technology was developed in order to obtain composites in the form of paper-like products containing almost 100% waste materials. Besides keratin, cotton linters, synthetic fibres and a resin were used during the experiments. The technology is based on paper manufacturing from pure cellulose pulp. The article describes the processing, structure properties and application of the new composites. One application of the composites confirmed by the Academy of Fine Arts in Warsaw - as a paper-like product for artistic painting - is presented.

Key words: *fibrous composite, paper-like products, keratin, chicken feathers, cotton linters.*

Intoduction

A great problem of the agriculture industry hitherto not entirely solved is managing the enormous amount of waste generated by poultry processing enterprises. It is estimated that more than 3 - 4 billion tons of feathers per year, mainly chicken feathers, are produced as a waste by-product by the world's poultry industry [1]. Unfortunately, feathers of almost 100% keratin are very difficult to biodegrade, and no methods are known to apply them on an industrial scale [2].

This was the reason that at the Institute of Biopolymers and Chemical Fibres (IBWCh), research work was undertaken into developing new structures, as a result of which various fibrous products and fibres with a keratin content were developed, characterised by different improved properties [3 - 8,], for example water retention.

However, in all these composites, keratin was used only in an amount of a few percent, showing no possibilities for significant re-use of waste in the form of feathers.

An entirely new conception was suggested to make an attempt at developing keratin-cellulose composites with a high percentage of keratin, which could be used as a paper-like fibrous product.

A review of international literature on this subject did not find any essential information. Therefore, this novel problem demanded intensive interdisciplinary research. Preliminary investigations [9, 10], carried out in the majority based on earlier experience, were finalised successfully and even allowed to obtain a patent. Considering this, a decision was made to develop a technology which could be the basis for obtaining different paper-like products of various applications, with a keratin content in the composite of at least 50 to 70%.

Theoretical considerations on the keratin structure led to the conclusion that from pure keratin, paper-like structures cannot be formed, confirmed experimentally by us [10] Keratin is a protein, a polymer with similar chains of its macrostructure, with amino-acid residuals and end-groups of NH and COOH, as well as sulphur complexes without the possibility to form hydrogen bonds between keratin elements, eventually activated by water. Keratin is a typical high hydrophobic compound [11]. On the other hand, contrary to them is the structure of cellulose, with its hydrogen bonds activated by water, which enables to form fibrous structures with fibres of a length of 1 - 6 mm, which can be processed into sheets, especially serving for the manufacture of paper. The strength of bonds between the fibres depends on the macromolecular structure of the particular cellulose, especially of the structure of surface layers. However, the use of additional bonding agents is often necessary. Paper is produced from cellulose pulp consisting of a mixture of cellulose with water and additional products, which is formed, impressed and dried. Commonly fir or birch cellulose is used, rarely cotton, and silk or even synthetic fibres as auxiliary components. It was clear that cellulose should be used in the mixture with keratin. The question was what kind thereof. After thorough considerations, cotton linters were chosen. Linters are by-products of processing cotton seers [8].

On the one hand, they are textile waste, but on the other they have many advantageous properties and are used pure or as an addition to paper pulp. They are used for increasing the sorption of water, porosity, durability and softness. Cotton linters are applied for manufacturing high-quality writing paper, paper for documents and banknotes, among others. The aim of the research presented herein was to develop a technology for producing fibrous paper-like composites composed of a high content of chicken feathers (of the range of more than 40%) and in this way offer a possibility for the managing and re-use of undesirable, difficult biodegradable waste [10].

Materials and methods

Materials

- Chicken feathers of white colour from the poultry slaughterhouse Wróblew 51, province Lodz, Poland, of the following composition:
  - a sulphur content of 2.9%,
  - a nitrogen content of 15.5%,
  - an ash content of about 1%.

  The data presented above as well as earlier [3] tests indicate that the amount of keratin in these chicken feathers is very high, up to about 100% of the mass of feathers. However, in this article, when we mention keratin content, we always mean the percentage of chicken feathers.
- Cotton linters prepared by Polish Security Printing Works, Warsaw, Poland

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The pulp of cotton linters contained fibres of 0.8 - 3 mm length and 19 µm width, composed of 98% cellulose, 1% hemicellulose, and 1% ash.

- Bicomponent synthetic fibres, core PET, Type T25 Biko flat 2.2 dtex from Trevira Company, Germany
- Kymene 20X resin from Hercules, Italy
- Ethyl alcohol
- Domestic surfactants ($Al_2(SO_4)_3$, NaOH).

In order to obtain a differentiated spectrum of a material for the manufacturing of paper-like composites for the initial experiments, the blends presented in table 1 were prepared.

All data are weight percentages of the products used for preparing the composite in relation to the final content.

Apparatus used

- Rapid-Köthen; VEB WERKSTOFF-PRÜFMASCHINEN Leipzing, Germany, Fabr nr 659/1,
- Laboratory band-forming machine; FRANK G. SCHÜRFELD § Co HAMBURG, Germany, KARL FRANK GMBH TYPE 897, MANNHEM-RHEINAU
- Hollander Valley; AB Lorentzen § Wettre Stocholm, Type 3-1 No 238.

Methods

Preparation of samples

Pretreatment of chicken feathers

The following steps were performed:

- removing all unnecessary substances from the poultry batch,
- washing with warm water at 40 °C in the presence of a surfactant, centrifugation,
- cutting them on a paper cutter into pieces of about 10 mm length,
- treating with ethyl alcohol for 24 h at room temperature in order to remove fat residues,
- drying in air at a temperature of 50 - 60 °C,
- disintegration by means of a hammer disintegrator.

Cotton linters were preliminarily processed according to the following procedure: The defibering process was carried out in a holender. The container of the defibriliser was filled with water and 400 g of cotton linters. The process was conducted without pressing the roller. The mass concentration was 1.6% at pH 6.8. Grinding was started after 15 min of disintegration by applying a load of 5.5 kg., carried out to a degree of 50 °SR. Next the slurry in an amount depending on the further processing was placed in a defibrator diluted with water in a proportion of 10 l water per 10 cm^3 slurry and mixed for 2 min. The slurry prepared was placed in the cylinder of Rapid-Köthen paper forming apparatus or destined for further processing with keratin.

The mass of the blends (keratin, linters, synthetic fibres, resin) was prepared depending on the composition, in general according to the following procedure.

The chicken feathers and cotton linters, preliminary prepared in an amount of 20% (50%, 60% etc.) keratin and 80% (50%, 34% etc) linters, were placed in a laboratory defibrerises. The concentration of the fibrous slurry was 0.72% (pH 6.8). Next (in some cases – see ***Table 1***) 3% of resin was added. From these blends, fibrous paper – like composites were formed on the Rapid-Köthen apparatus or on a laboratory band-forming machine. In the case of using blends with Trevira fibres, the latter were added to the Hollander.

The composite sheets were dried in a laboratory drier at a temperature of 90 °C (in the case of Trevira fibre addition to the composition at 130 °C).

The composite sheets were formed with a mass per square meter in the range of 50-140 g/m^2. The sheets from the Rapid-Köthen apparatus had the form of an oval with a smaller diameter of 20 cm. The paper web formed in the laboratory band-machine were formed with a width of 20.5 cm.

Determination of mechanical properties

- Mass per square meter (grammage), in g/m^2, in accordance with Standard PN-ISO 52-70: 1999, 10 samples tested,
- Tensile strength, in Nm/g, in accordance with PN-ISO – 52-70: 1999, 10 samples tested,
- Elongation, in %, PN-EN-ISO 1924-2:1998, 10 samples,
- Tear index, in mN, PN-EN 21974:2002, 8 samples,
- Burst index, in kPa·m^2/g, PN-EN ISO 2758:2005,
- Wet strength, in %, PN 84/P-50139, 20 samples.

Table 1. *Product content in the composite.*

Product, %			
Linters	**Keratin**	**Trevira**	**Resin**
100	-	-	-
80	20	-	-
77	20	-	3
67	-	30	3
47	50	-	3
40	50	10	-
37	50	10	3
31	66	-	3
-	67	30	3
-	70	27	3
-	70	30	-

All tests were carried out in the Laboratory of Paper Quality at IBWCh.

Water sorption and desorption

Sorption and desorption curves were recorded at room temperature by measuring the sample mass. At the beginning, the samples were placed in an exsiccator of 65% moisture (NH_4NO_3). After saturation and obtaining an equilibrium, the samples were placed in an exsiccator of 93% RH (KNO_3). After saturation at the new level, the samples were again set in 65% RH and the desorption was recorded (according to the procedure used for **testing the moisture absorption and desorption of polymer materials)**

Evaluation of the surface and cross-sections of the composite sheets were performed using a Quanta 200 SEM from FEI at a magnification of 2,000×. Structural investigations were performed under a high vacuum, in a natural state, and without gold sputtering. The area of the fibres' cross-section surface was measured with the use of the Analysis Docu software program from Soft Imaging System.

Organoleptic and application tests (typical assessment used by artists)

All these tests were carried out at the Department of Conservation and Restauration of Works of Art at the Academy of Fine Arts in Warsaw within a scope established for testing paper devoted to fine art. All tests were performed in a room at a temperature of 20 - 25 °C and humidity of about 50%.

In order to evaluate the samples, the following features were tested:

*Table 2. Mechanical prosperities of fibrous composites; * Not possible to measure composite breaks up.*

Pharameter	Composite		Content of chicken feathers in the composite. %							
	100% of keratin	100% cotton linters	20		50		66		70	
			+80% linters	+3% resin +77% linters	+50% linters	+3% resin +10% synt.fibres +2% linters	+3% resin +31% linters	+3% resin +10% synt.fibres +21% linters	+30% synt. fibrous	+3% resin +30% synt.fibres
Grammage. g/m^2	140	110	140	140	140	140	140	140	95.2	91.0
Tensile strength, Nm/g	*	36.2	5.67	7.49	2.436	16.5	-	41.3	2.99	5.85
Elongation, %	*	1.3	27.0	10.3	23.0	4.0	3.8	3.26	10.8	16.3
Tear index,mN	*	13.63	3.89	4.56	2.59	16.50	-	15.6	21.7	18.8
Burst index, kPam^2/g	*	1.55	0.292	0.364	0.775	0.257	0.72	0.52	0.70	1.26
Wet strength, %	*	-	11.9	22.3	3.8	41.6	40.5	43.3	98	97

- wet strength
- absorbability
- flexibility and mechanical strength after being soaked
- ease of application
- durability and colour saturation after being dried
- shrinkage after drying
- state of the paper surface after dryling
- smell.

Application tests consisted of painting the samples with water - colours, which were placed on a background of synthetic polymer and dried in a free state without using pressure. The techniques of water colours (aquarelle, guache) and acrylic paints were used.

Results and discussion

Mechanical properties

Selected mechanical properties are presented in ***Table 2*** and ***Figures 1, 2*** & ***3***. It should be emphasised here that the investigations were not carried out in order to explain the complex mutual relationships nor the cause of the influence of the composite content but to complete a range of data allowing to select suitable blends for further application. The highest keratin content possible, at accessible strength properties, especially a high wet strength, were the criterion of selection. The sorption properties and surface image were analysed in relation to the mechanical parameters. At first glance, ***Table 2***, with average values of the data (in general, test data with a dispersion of no more than ± 10%), gives an impression of chaotic data relations. Nevertheless, the following conclusions can be drawn:

- it is impossible to form usable sheets from pure keratin,
- pure linter sheets have good strength properties (without the values of wet strength),
- the addition of keratin to cotton liners, in general, lowers the strength properties. This is clearly visible in ***Figure 1*** (the point for 70% of keratin is related to an addition of synthetic fibres)
- the addition of resin, in general, slightly increases the strength data (only in

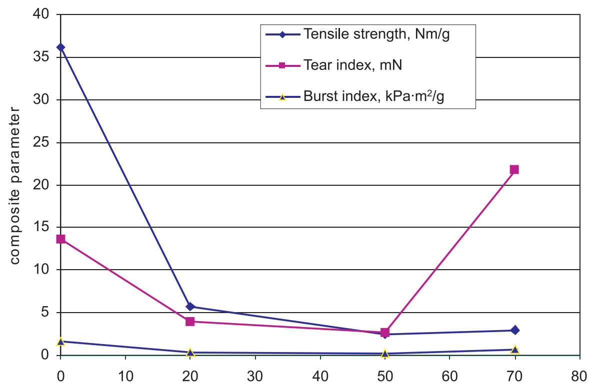

Figure 1. keratin content, %

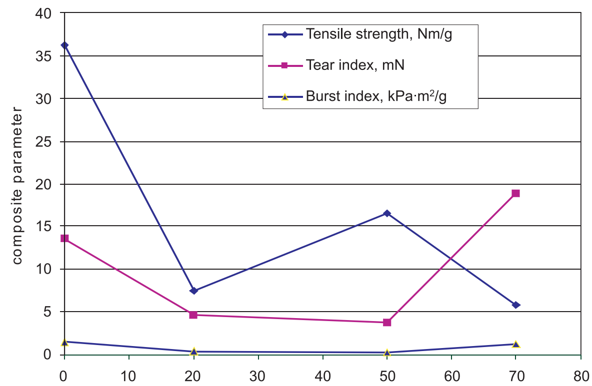

Figure 2. keratin content, %

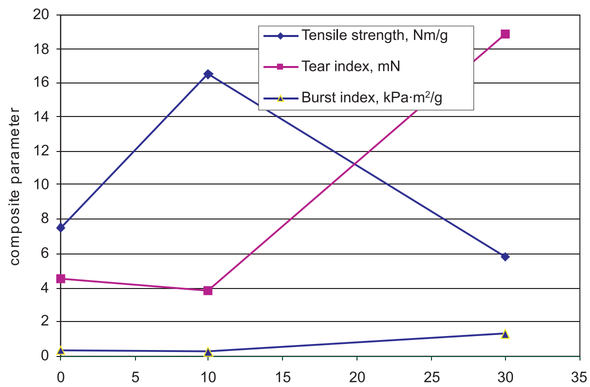

Figure 3. Trevira content, %

Figure 1. *Tensile strength, tear index, and burst index as a funktion of composite keratin content for fibres without resin content.*

Figure 2. *Tensile strength, tear index, and burst index as a funktion of composite keratin content for fibres with resin content.*

Figure 3. *Tensile strength, tear index, and burst index as a funktion of composite Trevira content.*

one case did the tensile strength significantly decrease)
- significantly higher wet strength values were characteristic of the sheets with the highest keratin content (which is very advantageous)
- the addition of bi-component synthetic fibres gives the advantageous impact of improving the composite strength properties
- the smallest elongations were shown by the pure linters sheets. The addition of keratin works in a strange manner - the highest elongation was characteristic of sheets with the highest keratin content (which in the case considered is rather disadvantageous).

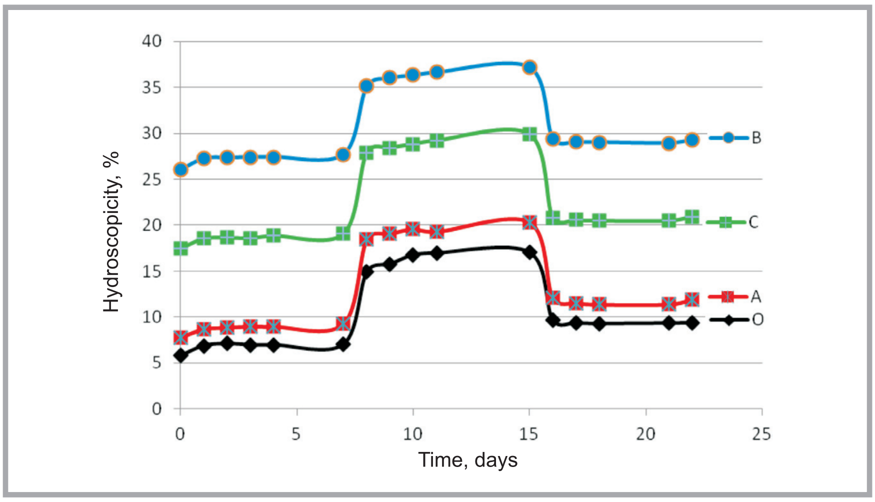

Figure 4. Sorption and desorption curves of the paper- like composites; Sample "O" - cotton linter sheets, Sample "A" - Composite sheets - like (50% keratin, 45% cotton linters, 5% synthetic fibers), Sample "B" - Composite sheets - like (50% keratin, 47% cotton linters, 3% resin), Sample "C" - Composite sheets - like (66% keratin, 34% cotton linters).

Considering the statements listed above, it could be concluded that from the point of view of mechanical properties, the composite sheets with the highest keratin content, within a range of 60 - 70% of keratin (chicken feathers), could be used as artistic paper for water printing.

Sorption and desorption properties

Selected curves are presented in ***Figure 4.***

Based on the curves, it was observed that the nature of the kinetics of the sorption and desorption processes was similar for all cases.

The sorption process under the condition of 65% RH was not intensive, and a greater jump did not appear until the samples were placed in an exsiccator of 93% RH. The highest absorbing capacity was observed for samples of pure cotton linter sheets. Keratin fibres are protein-based fibres, showing a tendency of hydrophobic behaviour. However, even the features of the composites with 66% of keratin seemed to be good enough for the application assumed.

Evaluation of the surface and cross-sections of samples

SEM photos of chicken feathers and sheets of various composition are shown in ***Figures 5 - 9***, presenting microscopic evaluation of the composite raw materials and sheets selected. The difference with respect to binding possibilities between pure feathers (***Figure 5.b***) and the composite containing 30% of bi-component synthetic fibres (***Figure 7***) is clearly visible.

In the SEM photos of keratin – linter composites, one can observe chicken feather particles differentiated by size (more visible on ***Figure 9***), as well as the better bonded cotton linters (***Figure 8*** and ***9***).

Organoleptic and application tests

After careful analysis of the tests performed, for further application tests as paper-like composites for artistic painting, the composites of 66% keratin were chosen, which was the highest accessible keratin content at relatively good properties, and at the same time offering a 97% waste content. The tests were carried out by observation of the processes of painting with water colours - during preparing the paper, the painting itself and the drying of the sheets, which were placed on plates of poly(methyl methacrylate) resin ("Plexiglas").

The following features could be noted

- *Wet strength*

The samples were characterised by a very high wet strength during painting. No significant complications during the application of water paints were observed. The paper did not become deformed or mechanically damaged. It was characterised by a relatively compact structure, resistant to any kinds of damage, which may arise during the binder application.

- *Absorbability*

The samples were characterised by medium hygroscopicity, and in order to wet the surface of the sheet, only a small amount of water should be used. To distribute water evenly, it was necessary to use appropriate brushes. The paper allows both spot-like and streak-like water deposition. The range of water penetration into the sheet structure depends on the duration of action, the amount of solvent and the tools used.

- *Flexibility and mechanical strength after being soaked*

The paper's properties in a wet state did not show negative trends but were not fully satisfactory for the painter. It was noted that the wet paper surface showed

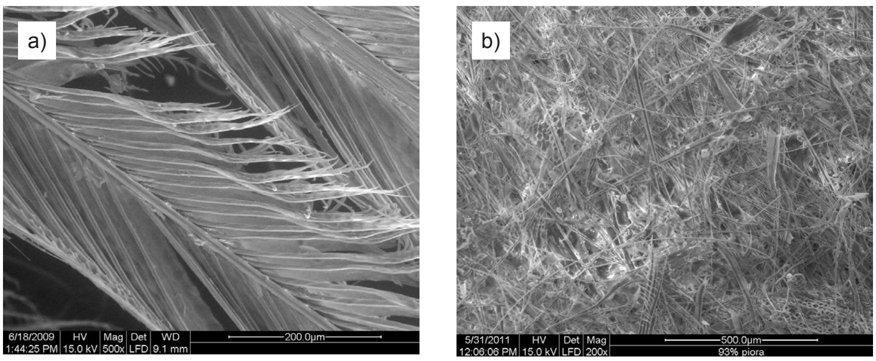

Figure 5. SEM photos of chicken feathers a) uncut b) cut.

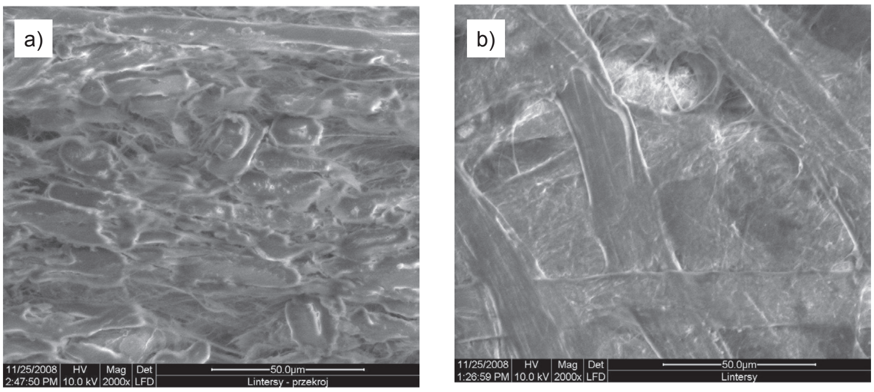

Figure 6. *SEM photos of a cotton linter sheet: a) cross-section, b) surface.*

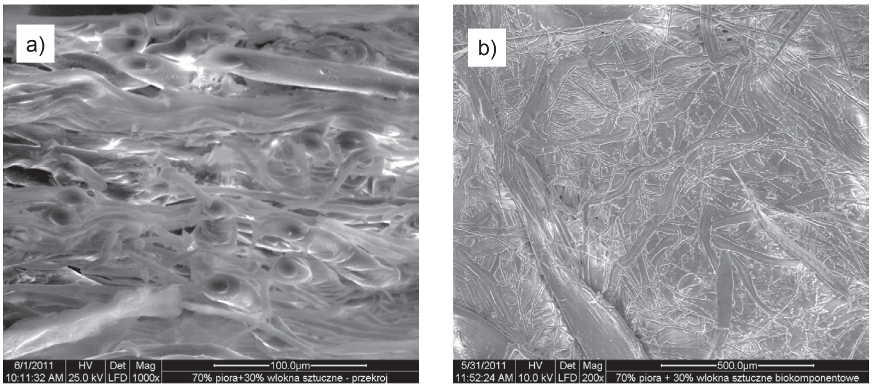

Figure 7. *SEM photos of composite sheet (70% chicken feathers and 30% synthetic fibres), a) cross-section, b) surface.*

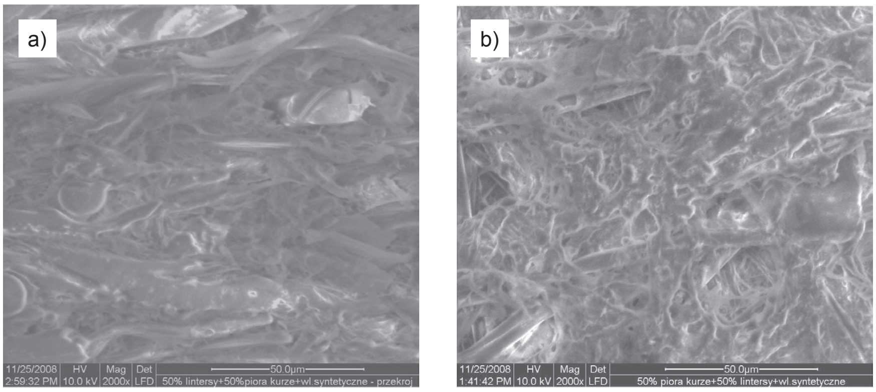

Figure 8. *SEM photos of the composite sheet (50% chicken feathers, 47%linters, and 3% synthetic fibres), a) cross-section, b) surface.*

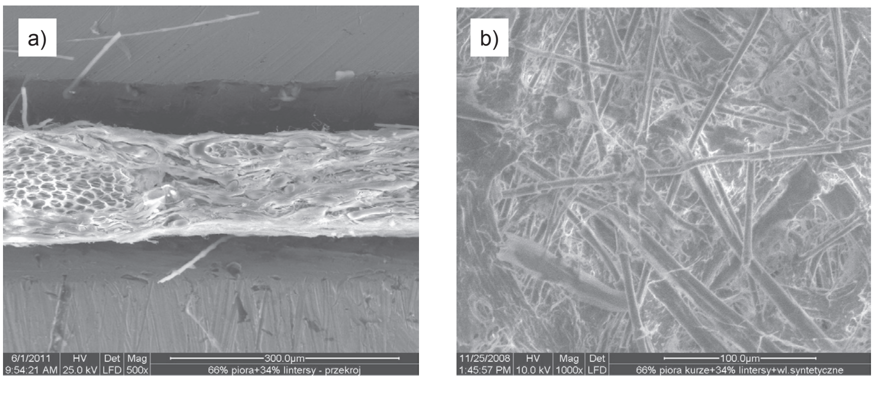

Figure 9. *SEM photos of composite sheet (66% chicken feathers, 3% resin, 30% linters and 4% synthetic fibres), a) cross-section, b) surface.*

good mechanical strength but had a tendency to "wipe up" passages heavily soaked, as a result of friction caused by brushes and other artistic tools.

- *Ease of paint application*

No obstacles were observed while transferring the water paints onto the sheet surface. The distinctive texture of the paint and the texture of the paper itself posed some resistance to the regular movement of the tool. But the paper absorbed the binder quite easily and was easily subjected to staining. Moreover, fairly slow drying was observed. Therefore, the slight "washing up" of paints by successive layers of the paint was observed.

- *Durability and colour saturation after drying*

The colour durability was high. The fading of acrylic and watercolour paints after drying was not observed which was probably the result of a weaker penetration of dyes into the structure of the paper and their better fastness to the surface.

- *Shrinkage after drying*

Paper deformation caused by moisture, transient as well as persistent was observed after drying. These changes were determined by the drying method without pressing the works. The resulting strain caused both linear and spatial changes. These deformations could be avoided if the works were pressed while drying.

- *State of the paper surface after drying*

After drying, the phenomenon of some surface "dust up" was observed, the scale of which rose depending on the amount of water incorporated into the structure of the paper while painting. However, such a phenomenon can also be observed in dry pastel pictures.

- *Smell*

No traces of the unpleasant, distinctive smell of wet feathers could be detect while applying paints on the surface of the paper composites, nor during drying.

The evaluation of the keratin/cellulose paper-like composites with respect to their application for artistic works, carried out using different water painting techniques (acrylic, gauche, aquarelle), allowed to state that although the composites did not meet all the expectations assumed by the painters, nothing essentially disadvantageous happened while painting, and that we obtained a very important material for artistic activity.

As regards the drawbacks and peculiarities of the new material, the artist must get accustomed to them through experience. The surface structure may even allow to create new possibilities of artistic impression. The great disadvantage of changes after drying can be omitted by pressing the composite over some periods while drying. Some drawings were obtained in this way, but it is necessary to elaborate procedures suitable for use in different cases.

Conclusions

- A technology was developed allowing to manufacture keratin fibrous composites with a very high, up to 70%, chicken feather content
- The technology enables to re-use chicken feathers, a very troublesome waste of the poultry industry, which is almost non-biodegradable and up to the present without serious possibilities of re-use.
- The technology concerns the manufacture of a range of fibrous paper-like composites, mainly keratin/cellulose blends but also keratin/synthetic fibre blends.
- Especially the use of keratin/cellulose blends with cotton linters as the cellulose content was confirmed. Paper-like sheets designed for use as material for artistic water - colour paintings were developed and evaluated positively. The paper-like composites offer great possibilities for original artistic creation.
- Additional future research is planned to eliminate some drawbacks of the composites, especially the changes in dimension while drying in a tensionless state, which at present demands the use of pressing the sheets over some periods of drying.
- Additional investigation are also planned in order to develop other applications of fibrous paper-like keratin composites.

Editorial Note

International and Polish authorities have evaluated the technology developed very highly. The Authors have been awarded, among others, by:

- *The Gold Medal Eureka - The Belgian and International Trade Fair For Technological Innovation, Brussels November 2009.*
- *The Gold Medal of International Invention Show & Technomart, Taipei 2010.*
- *Prize of the Polish Ministry of Science and Higher Education, Warsaw 2010.*
- *The Gold Medal Concours Lepine. LE Salon International de L'Invention de Paris, Paris 2011.*

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