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Chicken Feather-Containing Composite Non-Wovens with Barrier Properties

Abstract

The present study evaluated a method to prepare hydrophobic composite non-wovens containing chicken feathers and synthetic fibres (PES, PP). Such non-wovens can be made in aqueous medium using a paper-making method. The raw material (poultry feathers) is abundantly available from slaughterhouses as a waste. The sorption and mechanical properties and a morphological assessment of the prepared non-wovens are presented. The non-wovens were characterised by excellent sorption of a wide range of hydrophobic petroleum substances, good selectivity (sorption of liquids immiscible in water), and were unsinkable. The materials can be used directly on an aqueous surface, as well as on other surfaces such as concrete or asphalt to clean up leaked oily substances. The non-wovens are lightweight, easy to store and use and are inexpensive.

Key words: non-wovens, chicken feathers, keratin, composites, oil sorption.

Introduction

Protein waste has evoked the interest of scientists for many years. The material is attractive not only for uses in medicine and biotechnology, but also as a component of barrier materials. One of the least investigated and still not exploited protein waste materials is keratin-rich (ca. 95%) chicken feathers. Little attention has been paid to keratin so far. However due to its availability, abundance and properties, it has gained popularity as a potential component of composites combined with other biopolymers [1 - 9]. One problem arising with feathers is their proper collection in poultry slaughterhouses where they are difficult to manage. Every year, a huge amount of this material is generated worldwide, and since it is not biodegradable, it poses a serious burden to the environment. The poultry industry in Poland generates about 70,000 tons of such waste annually, offering a cheap raw material for many technical applications.

Poultry feathers are also a rich source of protein, which means that the material may become a sought-after component of biomass for uses in a variety of niche applications [10 - 14]. One interesting method of waste feather disposal is its use as a component of textile composites. For many years, new technological methods, including the paper-making method, have been investigated to form non-wovens with the aim of disposing of natural fibrous materials. Non-wovens cannot be prepared from feathers alone [17], but mixing with synthetic fibres (PP or PES) solves the problem. The papermaking technique is a method used to form paper-like materials with the use of non-cellulosic fibres which are not capable of bonding with other paper raw materials in a blend [15, 16]. However, the use of feather-originating fibres in this method has not yet been reported in the technical literature.

There is a recurring problem of crude oil leaks and effective methods are needed to neutralise these leakages. The present study investigates new non-wovens fabricated with chicken feather fibres that may contribute to solving this problem. The mechanism of action of the proposed non-wovens consists of providing a barrier that is impermeable to water but permeable to hydrophobic substances like crude oil and its derivatives, which are effectively absorbed by the feather component of the non-wovens. The nonwovens can be made entirely from waste; in addition to feathers, the other components, such as PP or PES (BIKO), can be of secondary grade or waste as well.

The use of feathers as a component in the fabrication of paper was patented by the present authors [17].

Aim of the work

The aim of the present work was to prepare non-wovens containing poultry feathers for use as a crude oil derivative-absorbing material. Feather fibres are made of keratin, which has a nano-porous structure and is an excellent material to absorb all sorts of oily substances [9, 12, 13]. Poultry feathers are made up of short fibres (0.5 - 2 cm). Therefore, the paper-making method operating in aqueous medium was selected for preparation of the non-wovens.

The planned outcome of the investigation was to prepare a new hydrophobic com-

posite in the form of non-wovens made of waste raw materials. The non-wovens were designed as an absorptive material to combat the effects of leakages of crude oil and other similar substances in water and on solid surfaces.

Materials

- Poultry feathers, white in colour, were obtained from a slaughterhouse (Wróblew, province of Łódź) after physical-mechanical processing. Physicalchemical characteristics:
 - Content of sulphur: 2.9%
 Content of nitrogen: 15.5%
 Content of ash: ca. 1%
 Content of fat: 15.8%
 - Apparent density: 3.5 x 10-2 g/cm³.
- Bicomponent PES staple fibre T254
 BIKO of the sheath/core type, length
 6 mm, linear density 2.2 dex, flat,
 semi-matte, used in the production of
 wet-laid non-wovens (supplied by the
 Trevira Co., Germany).
- 3. Polypropylene PP staple fibres, length 6 mm, linear density 15 dex (supplied by PPUH "VIOLA", Mirsk, Poland).
- Resin, hardenable in water, trade name Kymene 920, pH 4.5-8.5 (supplied by Hercules Co.) Kymene is a cationic resin (polyamido–polyamino–epichlorohydrine; PEE).

The PES BIKO fibre (low melting temperature, ca. 130 °C) and PP (inexpensive) fibre, which satisfy the requirements of the second component of the non-wovens, are hydrophobic staple fibres made of fusible resins.

Preparation of the non-wovens by the paper-making technique

Preparation of the fibres

Purified and screened fibres were washed three times in water at about 40 °C with a detergent for 1 h and then centrifuged for 10 min. The final phase of pre-processing was soaking 15% H₂O₂, after which the water was removed by centrifugation. The purified fibres were disintegrated by:

- cutting using a paper cutter
- grinding on a Sprout-Waldorom disk grinder, 0.3 mm slot.
- grinding on a Sprout-Waldorom disk grinder, 0.1 mm slot.

The dried fibres were shredded in a KMW 1953 disintegrator (Karlstad, Sweden).

Scanning electron microscopy was used to assess the appearance of the cut fibres. The cut fibre dimensions were measured using the software analySISDocu by Imaging System Co. The average thickness of the fibre was 5.0 μ m and the length was 30 - 60 μ m.

Preparation of the non-wovens by the paper-making technique

Preparation of the non-wovens from polypropylene (PP) fibres and poultry feathers

A non-wovens was manufactured by the paper-making technique in aqueous medium from a mixture of feathers and PP fibres in two versions:

- 50% feathers and 50% PP fibres.
- 70% feathers and 30% PP fibres.

For each of the variants, 5 non-wovens samples were prepared with the addition of 2% KYMENE 920 resin (in terms of the mass of the fibres). The mixtures were ground on a Sprout-Waldorom disk grinder with a 0.3 mm slot. Attempts to prepare non-wovens from a mixture of fibres without the resin were not successful. This is the reason why the Kymene 920 resin hardened in water was added. In experimental laboratory trials, the optimum amount of resin to be added and the concentration of the components in aqueous suspension were established. A 2% content of the resin (based on the mass of the fibrous components) and a concentration of 0.72% for the fibrous components in the aqueous suspension were adopted. The pH of the suspension was 6.8.

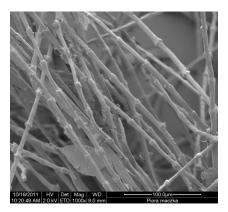


Figure 1. SEM image of poultry feathers used in the preparation of the non-wovens.

From the prepared suspension, sheets (with a diameter of 20 cm) of the non-wovens were formed using the Rapid-Köthen laboratory apparatus. The sheets were dried at 90 °C for 20 min and their physical-mechanical properties were tested according to published standards [18 - 29].

Preparation of the non-wovens from BIKO fibres and poultry feathers

Non-wovens were formed by the papermaking technique in aqueous medium from a mixture of feathers and BIKO fibres in two versions:

- 50% feathers and 50% BIKO fibres,
- 70% feathers and 30% BIKO fibres.

Trials were also performed to prepare the non-wovens with a low content of BIKO fibres (10 - 20%) calculated based on dry mass of the feathers. These attempts were unsuccessful; it appeared that consistent and durable non-wovens cannot be made with a low content of BIKO.

For the 50%/50% and 70%/30% versions, five samples each of the non-wovens were prepared with the addition of 2% of KYMENE 920 resin (based on the mass of the fibres).

The aqueous suspension of the ground feathers and BIKO fibres was introduced to a laboratory defibrator (CBTPP Type R-R) running at 1400 r.p.m. The content of the fibrous mass in the suspension was 0.72%; the pH was 6.8. To improve interfibre bonding, 2% water-hardenable resin KYMENE 920 was added. The amount of the resin to be added was established in previous investigations. From the prepared suspension, sheets (with a diameter of 20 cm) of the non-wovens were formed on the Rapid-Köthen laboratory apparatus. The sheets were dried at 90 °C

for 20 min and their physical-mechanical properties were tested according to published standards [18 - 29].

Testing methods

Assessment of the non-wovens properties

The non-wovens samples were assessed in the Laboratory of Paper Quality of the Institute of Biopolymers and Chemical Fibres (IBWCh) according to published standards [18 - 29].

Estimation of absorption capacity

A weighed amount of the non-wovens was put in an aqueous bath containing a known amount of oil. After 5 min, the sample was taken out of the bath, dried on filter paper under ambient conditions and the amount of the absorbed and retained oil was measured (in %).

Four different oils with various viscosities were used in this study:

- 1. Oil for vacuum pumps with a dynamic viscosity of 260 mPa·s.
- 2. Waste oil of vacuum pumps with a dynamic viscosity of 115 mPa·s.
- CASTROL 15W/40 GTX with a dynamic viscosity of 227 mPa·s.
- 4. Transol 68, a synthetic gear oil, with a dynamic viscosity of 175 mPa·s.

Estimation of oil viscosity

Dynamic viscosity was measured on a Brookfield numerical viscometer, model RV DV-II, with the following parameters:

- Temperature: -20 °C
- Time in thermostat: 15 minutes
- Cone: CPE-41
- Volume of tested sample: 2.0 cm³

Inspection of the non-wovens by scanning electron microscopy

A microscopic inspection was performed sung an SEM Quanta 200 by FEI Co (USA). The samples were sprinkled with gold powder in a vacuum with a vacuum sprayer (type Q 150R S) and inspected by SEM under high vacuum and at a voltage of 25 kV.

Results

The non-wovens made of the feathers and PP fibres, despite very good absorption capacity, had poor mechanical strength. Forming the non-wovens with this composition was considered unsuccessful.

Tables 1 - 3 and **Figures 1 - 9** show the physical-mechanical and sorption properties, as well as a morphological assessment of the non-wovens.

The tensile strength, extension, energy absorption during drawing, tear resistance and water fastness could not be measured in the feathers/PP non-wovens on account of poor mechanical resistance.

The lack of water absorption provides evidence of the hydrophobic nature of the material, a desired feature in feather-containing non-wovens. The material was selective in terms of sorption, as it retarded water but readily absorbed oily substances.

Assessment of the feathers/PP fibres non-wovens

- The non-wovens made with feathers and PP fibres using the paper-making process showed insufficient mechanical properties.
- Air permeability of the non-wovens with 50% PP fibres was ca. 6% lower than that of the PP fibre-containing material (30%).

Notwithstanding their poor strength, these materials had the desired absorption properties and they did not imbibe water but did imbibe oil.

Assessment of the feathers/BIKO fibres non-wovens

- An increase amount of the BIKO fibres in the non-wovens resulted in better strength and air permeability.
- With 50% of the BIKO fibre, the tear resistance was high and the cutting edge of the Elemendor apparatus did not cut the material. Tearing resistance is defined as the strength needed

Table 1. Properties of non-wovens made from feathers & PP fibres.

Ovality navameter	Test results				
Quality parameter	70% feathers/30% PP fibres	50% feathers/50% PP fibres			
Surface density, g/m ²	193.0	190.9			
Apparent density, g/cm ³	0.3	0.3			
Thickness, mm	0.6	0.6			
Absorption of water g/g *	no	no			
Air permeability L/m2*s	147.0	138.0			

Table 2. Properties of the non-wovens made from feathers & BIKO fibres.

Overlite measurement on	Test results				
Quality parameter	70% feathers/30% BIKO fibres	50% fibres/50% BIKO fibres			
Surface density, g/m ²	188	180.09			
Apparent density, g/m ³	0.38	0.22			
Thickness mm	0.49	0.79			
Tensile strength, N/m	824	920			
Extensibility, %	22.8	23			
Energy absorption during drawing J/m ²	102.5	124.3			
Tear resistance, mN	2200	No tear			
Burst resistance, kPa	186	130			
Water fastness, %	99	99			
Absorption of water, g/g (*)	no	no			
Air permeability, L/m2*s	418	605			

to execute tearing to a certain distance of a previously incised sample of a paper material (PN-EN ISO 2759:2005, range 50-3200 m*N).

Good tear resistance is desired in paper materials that are exposed to tearing, such as packaging materials, labels, newspaper, etc.

- The non-wovens did not imbibe water (it was hydrophobic).
- The non-wovens revealed high water fastness (99%); that is, the ability to sustain mechanical strength after saturation with water.
- Both non-wovens showed good dimensional stability. A tested sample of

the non-wovens maintained its original dimensions and thickness after 48 hours at 23 °C and 90% relative air humidity.

Assessment of the absorption properties of the non-wovens

Imbibition tests were performed with selected oils to assess the suitability of the hydrophobic non-wovens for use as an absorption material for crude oil-derived substances. The results are shown in *Table 3*. All the prepared non-wovens made of feathers and synthetic fibres (PP and BIKO) showed excellent absorption of crude oil-derived substances and did not imbibe water. They meet the demands of a hydrophobic material used to absorb oils and other petroleum substances.

Table 3. Absorption of oils by the composite non-woven material.

Composition of the non- woven material	Type of oil								
	1.		2.		3.		4.		
	Viscosity 260 mPa·s		Viscosity 115 mPa·s		Viscosity 227 mPa·s		Viscosity 175 mPa⋅s		
	Mass of oil, g	Oil absorption, %	Mass of oil, g	Oil absorption, %	Mass of oil, g	Oil absorption, %	Mass of oil, g	Oil absorption, %	
PP 100%	0.89	40	0.91	55	0.79	36	0.93	56	
50% feathers/50% PP fibres	0.98	99	0.98	99	0.98	89	0.98	96	
70% feathers/30% PP fibres	0.96	100	0.96	100	0.95	100	0.99	100	
100% BIKO	0.73	38	0.76	40	0.87	35	0.93	58	
50% feathers/50% BIKO fibres	0.94	97	0.96	100	0.90	99	0.91	89	
70% feathers/30% BIKO fibres	0.98	98	0.97	99	0.97	100	0.98	90	

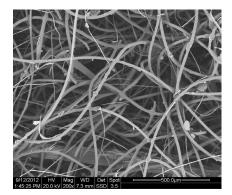


Figure 2. SEM image of the non-wovens surface; 50% feathers & 50% BIKO.

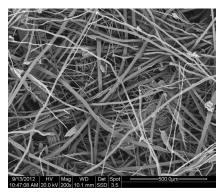


Figure 3. SEM image of the non-wovens surface; 50% feathers & 50% PP.

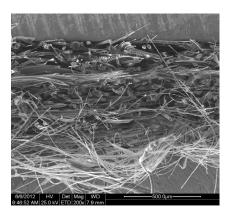


Figure 4. SEM image of the non-woven cross-section; 50% feathers & 50% BIKO.

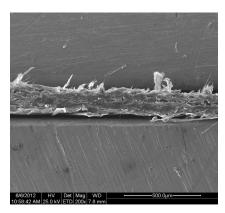


Figure 5. SEM image of the non-woven cross-section; 50% feathers & 50% PP.

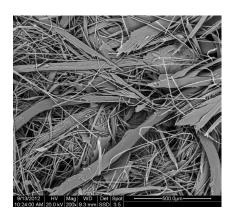


Figure 6. SEM image of the non-wovens surface; 70% feathers & 30% BIKO.

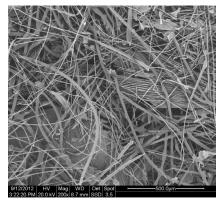


Figure 7. SEM image of the non-wovens surface; 70% feathers & 30% PP.

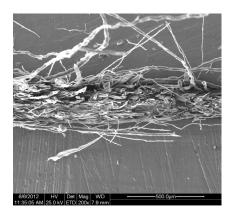


Figure 8. SEM image of the non-woven cross-section; 70% feathers & 30% BIKO.

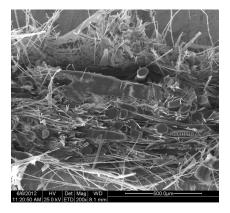


Figure 9. SEM image of the non-woven cross-section; 70% feathers & 30% PP.

Morphological assessment of the non-wovens by scanning electron microscopy

Scanning electron microscopy was used to assess the appearance and cross-section of the non-wovens. Images of the surfaces and cross-sections are shown in *Figures 2 - 9*.

From the comparison of non-wovens surfaces containing 50% feathers and 50% of the PP or BIKO fibres (Figures 2 and 3), the BIKO-containing material (Figure 2) had higher porosity. Figures 4 and 5 depict the cross-sections of the same non-wovens. The BIKO-containing material (Figure 4) showed a looser structure of the two components in agreement with the higher porosity than the PP-containing material (Figure 5). From the comparison of non-wovens surfaces containing 70% feathers and 30% PP or BIKO fibres (Figures 6 and 7), the BIKO-containing material (Figure 6) had higher porosity. It cannot be univocally stated that a relationship exists here between the porosity of the structure and the sorption of oil.

The differences in the cross-sections of the non-wovens presented in *Figures 8* and *9* cannot be explained univocally. PP fibres are hydrophobic, while polyester BIKO fibres are weakly hydrophilic. The formation of the non-wovens was performed in aqueous medium and the packing of the two synthetic fibres against the feather fibres was different. This may be the reason for the difference in the internal structure as seen in the SEM images.

From the comparison of the surfaces of the non-wovens with 50% feathers (Figures 2 and 3) and those containing 70% feathers (Figures 6 and 7), it seems that an increase in the content of feathers caused a decrease in porosity.

Conclusions

It was demonstrated in these investigations that the possibility exists of preparing composite non-wovens from poultry feathers and synthetic fibres (PES and PP) using a paper-making method in aqueous medium. All of the prepared non-wovens satisfied the expectations of a hydrophobic material with an excellent ability to absorb oily substances. Moreover, the non-wovens made of feathers and BIKO fibres showed very good mechani-

cal properties. The PP fibre-containing non-wovens had insufficient mechanical strength but showed equally good sorption properties.

The newly prepared materials present an opportunity to utilise the burdensome and not biodegradable waste feathers generated by the poultry industry. These non-wovens have the ability to absorb a wide range of hydrophobic crude oilderived substances that are immiscible in water. These materials may be used regardless of weather conditions on a water surface or any other surface like concrete or asphalt. These products are lightweight, easy to store and use, and are inexpensive.

References

- Rouse JG, Van Dyke ME. A review of keratin-based biomaterials for biomedical applications. *Materials* 2010; 3(2): 999-1014.
- Balaji S, Kumar R, Sripriya R, Rao U. Characterization of keratin–collagen 3D scaffold for biomedical applications. Polym. Adv. Technol. 2011;
- Wrześniewska-Tosik K, Adamiec J. Biocomposites with a content of K from chicken feathers. Fibres & Textiles in Eastern Europe 2007; 1(60): 106-112,
- Wrześniewska-Tosik K, Wawro D, Stęplewski W. Szadkowski M. Fibrous products with keratin content. Fibres & Textiles in Eastern Europe 2007; 2(61): 30-35.
- Wrześniewska-Tosik K, Wawro D, Ratajska M, Stęplewski W. Novel biocomposites with feather keratin. Fibres & Textiles in Eastern Europe 2007; 5-6(64-65): 30157-162.
- Wrześniewska-Tosik K, Kucharska M, Wawro D. Fibrous keratin-containing composite. Fibres & Textiles in Eastern Europe 2008; 6(71): 114-116.
- Wawro D, Stęplewski W, Wrześniewska-Tosik K. Preparation of keratin-modified chitosan fibres. Fibres & Textiles in Eastern Europe 2009; 4(75): 37–42.
- Aluigi A, Varesano A, Montarsolo A, Vineis C, Ferrero F, Mazzuchetti G. Electrospinning of keratin/poly(ethylene oxide)blend nanofibers. *J Appl Polym Sci.* 2007; 104: 863–70.
- Aluigi A, Vineis C, Varesano A, Mazzuchetti G, Ferrero F, Tonin C, Structure and properties of keratin/PEO blend nanofibres. *Eur Polym J*. 2008; 44: 2465– 2475.
- Filshie BK, Rogers GE. An electron microscope study of the fine structure of feather keratin. *J Cell Biol* 1962; 13(1): 1-12.

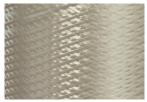
- Chen C, Chuanbao C, Xilan M, Yin T, Hesun Z. Preparation of non-woven mats from all-aqueous silk fibroin solution with an electrospinning method. *Polymer*. 2006; 47(18): 6322-7.
- Kar P, Misra M. Use of keratin fiber for separation of heavy metals from water. J Chem Technol Biotechnol 2004; 79: 1313-1319.
- Hong CK, Wool RP. Development of a bio-based composite material from soybean oil and keratin fibres. *J Appl Polym Sci* 2005; 95(6): 1524–1538.
- Chojnacka K, Górecka H, Michalak I, Górecki H. A review: valorization of keratinous materials. Waste Biomass Valor 2011; 2: 317-321.
- 15. Szwarcsztajn E. *Preparation of paper pulp* (in Polish). Warszawa PWT 1991.
- Wdowiak T. Technology to produce nonwoven by a paper-making method (In Polish). Przegląd Papierniczy 1970; 94.
- Wrześniewska-Tosik K, Marcinkowska M, Wawro D, Mik T, Pałczyńska M. Paper-like materials with poultry feather content. P. 386,554. Poland 2008.
- PN-EN ISO 536: 2012: Paper and paperboard – Estimation of surface density
- PN-EN ISO 534: 2012: Paper and paperboard - Estimation of thickness, apparent density and specific volume.
- PN-EN ISO 1924-2: 2010: Paper and paperboard - Estimation of properties under the action of drawing strength.
- PN-EN ISO 5270: 2011: Fibrous pulps— Laboratory sheets - Estimation of physical properties.
- PN-EN ISO 5269-2: 2005: Fibrous pulps

 Preparation of laboratory sheets for physical testing -- Part 2: Rapid –Köthen method.
- PN-EN ISO 1974: 2012: Paper Estimation of tearing resistance Elmendorf method.
- 24. PN-EN ISO 2758: 2005: Paper Estimation of bursting resistance.
- PN-P-55072: 1982: Useful properties of printing materials - Estimation of paper dusting.
- 26. PN-89/P-04781/12: Fibrous dressing materials Estimation of water imbibition
- PN-P-50176-3: 1994: Paper and paperboard - Estimation of air permeability (medium range) - Bendtsen method.
- 28. PN-P-50139: 1984: Paper products Estimation of breaking strength in wet condition, and water fastness.
- PN-EN 1602:1999: Materials for thermal construction insulation - Estimation of apparent density.
- Received 06.07.2012 Reviewed 22.10.2012



Multifilament Chitosan Yarn

The Institute of Bioploymers and Chemical Fibres is in possession of the know- how and equipment to start the production of continuous chitosan fibres on an extended lab scale. The Institute is highly experienced in the wet - spinning of polysaccharides, especially chitosan. The Fibres from Natural Polymers department, run by Dr Dariusz Wawro, has elaborated proprietary environmentlyfriendly method of producing continuous chitosan fibres with bobbins wound on in a form suitable for textile processing and medical application.



Multifilament chitosan yarn

We are ready, in cooperation with our customers, to conduct investigations aimed at the preparation of staple and continuous chitosan fibres tailored to specific needs in preparing non-woven and knit fabrics.

We presently offer a number of chitosan yarns with a variety of mechanical properties, and with single filaments in the range of 3.0 to 6.0 dtex.

The fibres offer new potential uses in medical products like dressing, implants and cell growth media.