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# Films and Non-wovens Coated by Chitosan for Special Applications: Biological Decomposition Aspect

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## Abstract

The utilisation of sanitary products in the context of increasing amounts of household waste is a very important question. Their lack of susceptibility to biodegradation generates great social and environmental problems. This article presents the results of tests aimed at devising biodegradable non-woven fabrics which would be characterised by sufficient strength and the ability to disintegrate quickly in a water environment. The non-woven fabrics were obtained from polypropylene or viscose fibres with the use of buffered chitosan salt as a binding agent. The obtained results of ground & water degradation and the respirometric test encourage the use of modified non-woven fabrics in the production of disposable hygienic products.

**Key words:** non-woven, chitosan forms, biodegradation.

## Introduction

A most important problem in the manufacture of sanitary products is the disposal of sanitary pads, nappies and towels after use. The man-made non-wovens used for the manufacture of last-generation disposable products are mostly not susceptible to biodegradation. Sanitary products may make up as much as 50% of the waste from household goods. They should never be flushed down toilets, as this causes blocked household drains and maintenance problems at sewage treatment plants. The cost to each local authority of disposing of these products runs into hundreds thousands of dollars per year, so sanitary products schemes now play a key role in local authorities' waste disposal strategies.

The idea of introducing a non-woven that indicates necessary endurance during use and will easily disintegrate after use is still a major priority of the sanitary industry sector. In the Institute of Chemical Fibres (at present the Institute of biopolymers and Chemical fibres) we have developed non-wovens employing chitosan for use as sanitary products [1].

Chitosan and its derivatives are often used for preparation of biodegradable films. The use of chitosan in the form of salt causes the solubility of the formed films in a solution of pH < 7. However,

an application of the microcrystalline form of this biopolymer shows resistance to dissolution at neutral pH, as well as prolongation of biodegradation due to the relatively high crystallinity of the films formed.

The aim of this study was to determine the effect of the application of chitosan lactate as a modification of various types of non-wovens on their susceptibility for biodegradation.

## Materials and methods

### Materials

#### Chitosan

The chitosan was made by Vanson Ltd. (USA). The properties of biopolymer used are presented in Table 1.

#### Oriented fibre webs

For the preparation of non-wovens, two types of sources, of synthetic and natural origin (polypropylene: PP non-woven and viscose: VS non-woven), were used:

- oriented polypropylene fibre web, used for the manufacture of the non-wovens with a surface weight of 20 and 50 g/m<sup>2</sup>;
- oriented viscose fibre web, used for the manufacture of non-wovens with a surface weight of 20 and 50 g/m<sup>2</sup>;

**Table 1.** Properties of chitosan used;  $\bar{M}_V$  – average molecular weight; DD – degree of deacetylation; WRV – water retention value,<sup>1)</sup> – heavy metal content determined by PN-82/C-84002.15 Standard, <sup>2)</sup> – ash content determined by ISO 3451-1:1997 Standard.

Symbol of samples	Form	$\bar{M}_V$ , kDa	DD, %	WRV, %	Solubility in 1% acetic acid, wt%	Moisture content, wt%	Heavy metal content <sup>1)</sup> , wt%	Ash content <sup>2)</sup> , wt%
V3	Powder	166.3	76.2	121.0	100	7.8	0.005	0.3

### Other materials

Glycerol anhydrous pure p. a.  
Lactic acid 80% pure p. a.  
Acetic acid 80% pure p. a.  
Hydrochloric acid pure p. a.  
Sodium hydroxide pure p. a.  
Ceramzit, a gardening bed used for plant cultivation  
Standard soil

### Analytical methods

#### Characterisation of chitosan used

The degree of deacetylation (DD) of chitosan was determined by potentiometric titration [2]; the average molecular weight ( $M_V$ ) by viscometry [3, 4]; and the water retention value (WRV) by the gravimetric method [3].  $M_V$  and DD of microcrystalline chitosan (MCCh) were determined by the modified method described in [3, 4].

#### Determination of chitosan lactate content in modified non-wovens

The chitosan lactate content in the modified non-wovens was determined by the gravimetric method. The modified non-wovens were immersed in a 1% (v/v) acetic acid solution for 12 h with continuous shaking. The non-wovens were separated and washed with 500 ml of distilled water. The procedure was repeated twice. Next, non-wovens were dried at 105 °C to a constant weight. The percentage of bonding agent content was calculated as a ratio of the initial weight of the modified non-woven to the non-woven weight obtained after removing the chitosan lactate.

### Biological decomposition

#### Mineralisation test

The biological decomposition of modified non-wovens and chitosan films was carried out in aqueous conditions (the mineralisation test) as well as in soil [5 - 8].

Biological decomposition in aqueous conditions in communal waste (the mineralisation test) was carried out in glass reactors containing the following elements:

- samples of the non-woven being investigated,
- a wide range of micro-organisms susceptible for sample degradation originated from the sewage-treatment plant in Swiecie (Poland), as well as soil.
- aqueous media containing microelements such as: Fe, P, S, Mg, N, etc. The microelements were introduced

into the decomposition bath in the form of salt solutions.

The process of biological decomposition was carried out in condition of carbon craving; the samples investigated were the sole source of carbon.

We used samples of rectangular shapes and comparable weights in series. The weight of samples were as follows:  $0.125 \pm 0.015$  g for chitosan films,  $0.450 \pm 0.05$  g for PP non-wovens, and  $0.500 \pm 0.05$ g for viscose non-wovens.

The decomposition process was conducted at a temperature of  $22 \pm 1$  °C in continuous shaking and aeration. The starting inoculum was counted as  $7 \times 10^6$  cfu/cm<sup>3</sup>, and the pH of the medium was 7.2. After each period of decomposition, the samples were decontaminated using a 3.0% solution of H<sub>2</sub>O<sub>2</sub>, deproteinised by a 0.5% solution of sodium hydroxide and dried. The samples' loss of weight was determined gravimetrically.

#### Respiratory test

The samples investigated were kept with the inoculum in the reaction vessel (3 dm<sup>3</sup>, containing a manometer). The reactor vessel with contents similar to that described in the previous section were continuously shaken and aerated in CO<sub>2</sub>-free air ( $0.5 \pm 0.1$  dm<sup>3</sup>/h). The conditions of the respiratory test were similar to those described in the previous section. The samples were powdered in an atmosphere of liquid nitrogen before being introduced into the reactor. The weight of each sample was 500 mg. The

volume of the CO<sub>2</sub> which was emitted during the metabolic process of sample decomposition by micro-organisms responded to the biodecomposition degree was measured. The test was carried out up to the total disintegration of the sample, which was noted when the relationship between the volume of CO<sub>2</sub> and the time of the test showed a plateau. The volume of the CO<sub>2</sub> produced by micro-organisms was determined using the titration method.

#### Decomposition in soil

The biological decomposition of the samples investigated was carried out in containers with perforated bottoms. The glass balls, the mixture of soil, the ceramzit, the sample being investigated and more soil were placed layer by layer. The constant temperature level of  $22 \pm 1$  °C and the soil humidity of 65% were maintained. After the test was finished, the samples were purified as described in the previous section. The general appearance of samples was visually estimated.

### Methods

#### Preparation of chitosan salt solutions

2.4 g of chitosan was dispersed in distilled water (150 ml) for 24 h. Then suitable amounts of acetic acid, lactic acid and hydrochloric acid were added to obtain final concentrations of 0.8%; 0.8% and 0.2% respectively. The chitosan solution was filtered using cheese-cloth and filled up to 200 ml by distilled water. Next, a suitable amount of 1% (w/v) sodium hydroxide was dropped into it until the

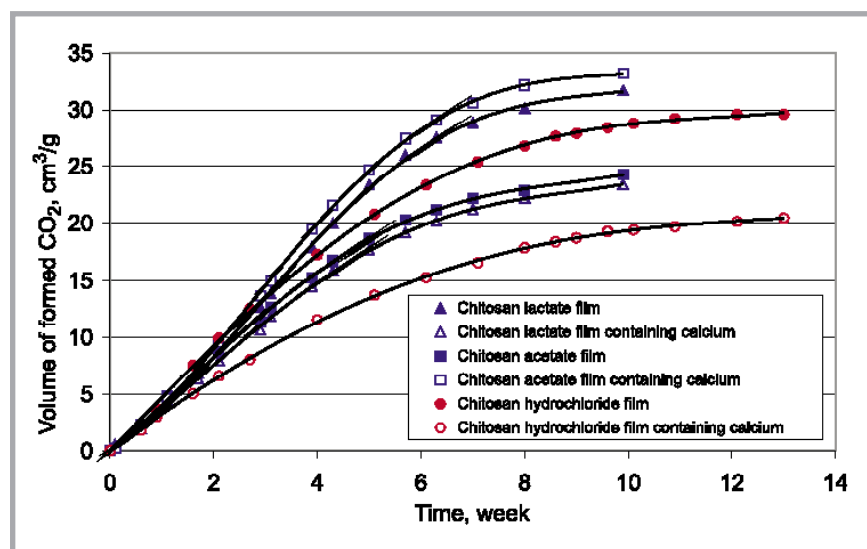


Figure 1. Volume of CO<sub>2</sub> emitted from chitosan salts films with or without calcium during biodecomposition test in aqueous condition.

pH fell within the range of 5.4 - 5.5. The buffered solution was filled with distilled water to 240 ml [1].

#### Preparation of chitosan salt solutions containing calcium

0.1 g of calcium chloride ( $\text{CaCl}_2$ ) was dissolved in 100 ml of solution made as described above [1].

#### Preparation of films

Buffered chitosan salt films with or without calcium were formed using the above-described solutions by air-drying on a PTFE plate (around  $6 \times 4 \times 0.3$  cm in size) for around 24 hours [1, 10].

#### Preparation of modified non-wovens in an aqueous chitosan lactate solution

Oriented fibre webs (made of polypropylene and viscose) were submerged in an aqueous chitosan lactate solution buffered to pH = 5.4 for 5 min. The excess of binding agent was impressed using the Fulard apparatus with a gap of 0.25 mm. Then the non-woven formed was dried in an oven for 24 h at 40 °C [9].

### Results and discussion

The criteria for selecting the best modified non-wovens regarding physical parameters such as surface weight (according to standard PN-EN 29073-1:1994), thickness (standard PN-EN ISO 9073-2:2002) tensile strength and elongation at break (standard PN-EN 29073-3:1994) as well as swelling behaviour in distilled water, synthetic urine and synthetic blood (standard DIN 53923) have been described in [1, 10, 11].

#### Respiratory test

##### Films made of various buffered solutions of chitosan in organic and in-organic acid

Figure 1 shows the volume of  $\text{CO}_2$  emitted during biodecomposition from chitosan salt films.

The greatest susceptibility for the biodecomposition was shown by the films made of buffered chitosan lactate solution, whereas the films prepared using chitosan hydrochloride solution containing calcium had the lowest rate of biodecomposition. Introducing calcium affected the decrease in the susceptibility to biodecomposition in communal wastes. As for usable properties for hygienic application, the most important factor is biodegradability. The buffered to pH = 5.4 solution of chitosan lactate was used as a binding agent for the manufacture of VS nonwovens.

##### Chitosan lactate modified non-wovens

The content of chitosan lactate onto modified non-wovens differed in relation to the type of source used.

Table 2 shows the content of chitosan lactate determined in modified PP and VS non-wovens.

Applying chitosan lactate to modify VS oriented fibres resulted in the chitosan salt content ranging from 10.7 to 18.8 % (w/w), successively for initial surface weights of 20  $\text{g}/\text{m}^2$  and 50  $\text{g}/\text{m}^2$ , whereas the application of PP oriented fibres yielded a chitosan lactate content of 5.7 % (w/w) for a non-woven initial surface weight of 20  $\text{g}/\text{m}^2$  and 11.1 % (w/w) for an initial surface weight of 50  $\text{g}/\text{m}^2$ .

The susceptibility to biodecomposition in communal wastes was determined in two

Table 2. Content of chitosan lactate determined in both the modified non-wovens made of PP and VS fibres.

Initial surface weight Type of non-woven	20 $\text{g}/\text{m}^2$	50 $\text{g}/\text{m}^2$
PP non-woven	5.7	11.1
VS non-woven	10.7	18.8

types of VS nonwovens which differed in surface weight and were modified by buffered chitosan lactate. The modified VS non-woven with a lower initial surface weight (20  $\text{g}/\text{m}^2$ ) showed a higher susceptibility for biodecomposition (Figure 2). It disintegrated almost completely over 6 weeks, whereas the modified VS non-woven with higher surface weight (50  $\text{g}/\text{m}^2$ ) indicated a 4% initial residue over the same period of biodecomposition.

The volume of  $\text{CO}_2$  indicated 8% to 15% higher secretion for VS non-wovens with a surface weight of 50  $\text{g}/\text{m}^2$  compared to the modified VS non-woven with an initial surface weight of 20  $\text{g}/\text{m}^2$  (Figure 3). This phenomenon is probably connected with the higher amount of chitosan lactate introduced with the VS non-woven with the higher initial surface weight into the test reactor.

The general appearance of the VS non-wovens with a surface weight of 20  $\text{g}/\text{m}^2$  and 50  $\text{g}/\text{m}^2$  and modified by chitosan lactate is shown in Figure 4.

#### Biodegradation in soil

##### Films made of various buffered solutions of chitosan in organic and inorganic acid

All films prepared from the solution of chitosan lactate buffered to pH = 5.4 were

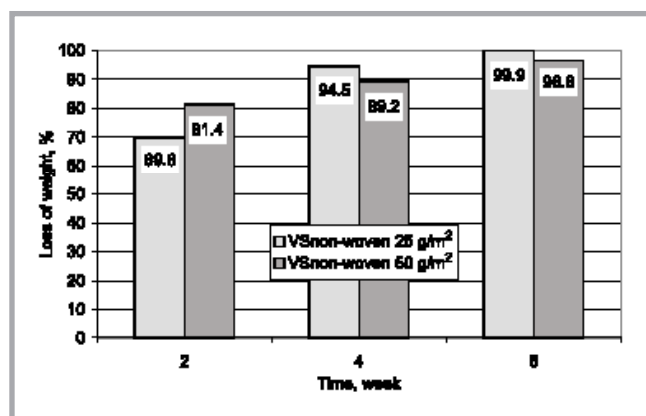


Figure 2. Loss of weight of chitosan lactate modified VS nonwovens (initial surface weight: 20  $\text{g}/\text{m}^2$  vs. 50  $\text{g}/\text{m}^2$ ) during biodecomposition in communal wastes.

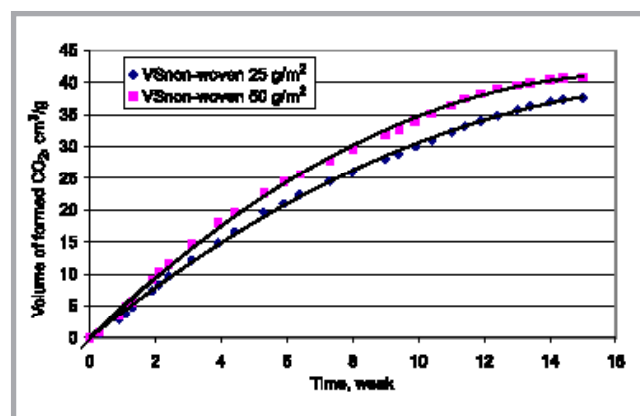


Figure 3. Volume of  $\text{CO}_2$  evolved from chitosan salt-modified VS non-wovens (20  $\text{g}/\text{m}^2$  vs. 50  $\text{g}/\text{m}^2$ ) during biodecomposition in aqueous conditions.

disintegrated in soil for no longer than 2 days after introduction (Figure 5). Application of anything other than lactic acid solvent resulted in a prolongation of the disintegration time in soil (Figure 6 – 7).

Based on the soil decomposition test, the VS – and PP non-wovens have been modified by the solution of chitosan lactate buffered to pH = 5.4.

#### Non-wovens modified by chitosan lactate

The structure of modified non-wovens, both those made of viscose and those made of polypropylene fibres, underwent disintegration over 30 days of a soil test.

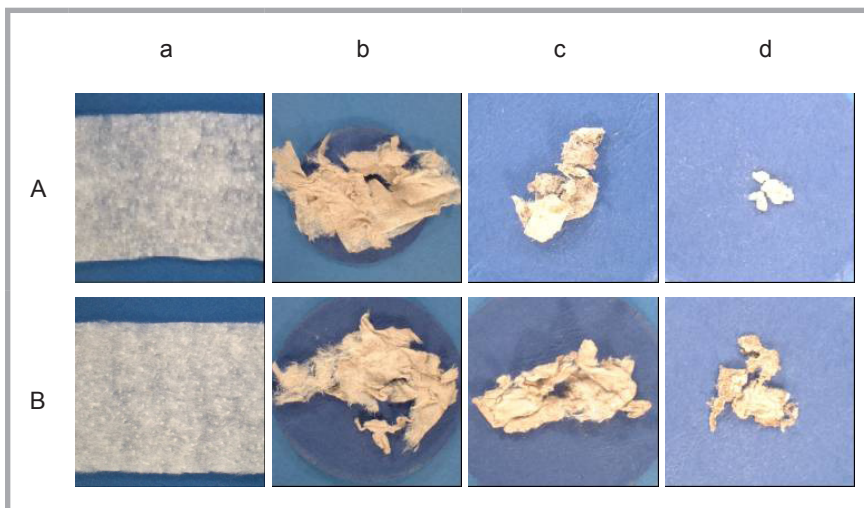
The colonisation of micro-organisms onto the fibres was found at the end of the test, except for in the modified PP non-woven, where the colonisation appeared during first 30 days of the test (Figure 8). VS non-wovens modified by a buffered solution of chitosan lactate were disintegrated and degraded more dynamically, both for those with a surface weight of 20 g/m<sup>2</sup> and those of 50 g/m<sup>2</sup> (Figure 9). VS non-wovens with a surface weight of 20 g/m<sup>2</sup> underwent almost total degradation after 8 weeks, whereas the residue of VS non-woven with a surface weight of 50 g/m<sup>2</sup> weighed around 15% of their initial weight.

#### Conclusions

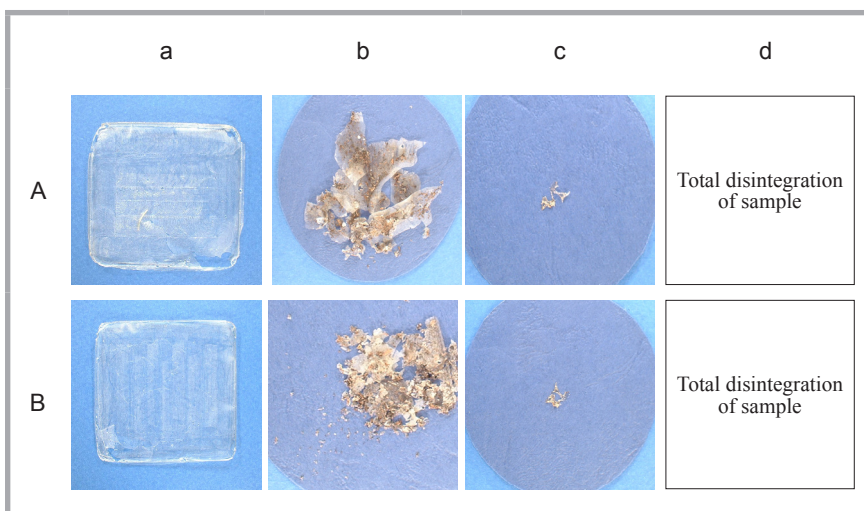
The presented study forms the basis for the application of novel, modified non-wovens for disposable products, and has drawn the conclusions given below:

- the highest rate of biodegradation of chitosan films was noted for films made of a solution of chitosan lactate buffered to pH = 5.4;
- viscose (VS) non-wovens modified by chitosan lactate showed better affinity to biodegradation than the polypropylene (PP) non-woven. Moreover, the colonisation by micro-organisms of modified polypropylene non-woven after the first month of the soil test was noted.

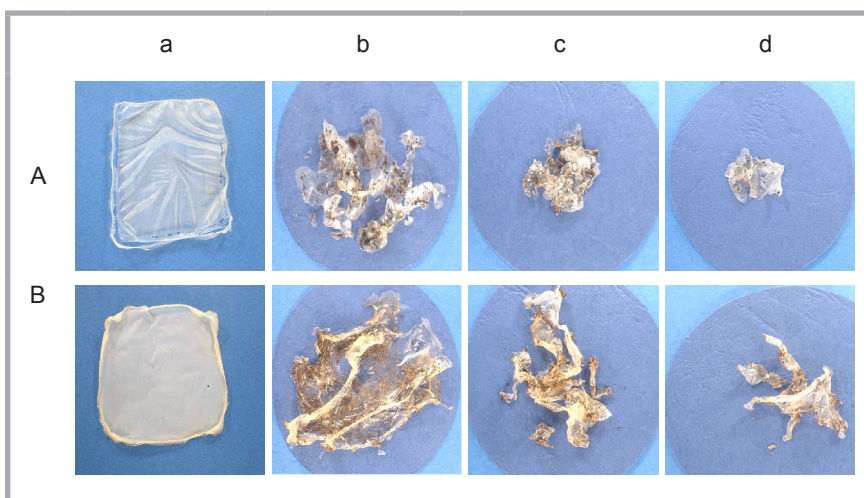
Non-wovens modified with chitosan salts seem to be a promising source for use in disposable sanitary products because it is possible to control the properties of non-wovens by various forms of chitosan and improving in biodegradability. The elaborated non-wovens containing chitosan lactate as a bonding agent meet the requirements for hygienic devices,



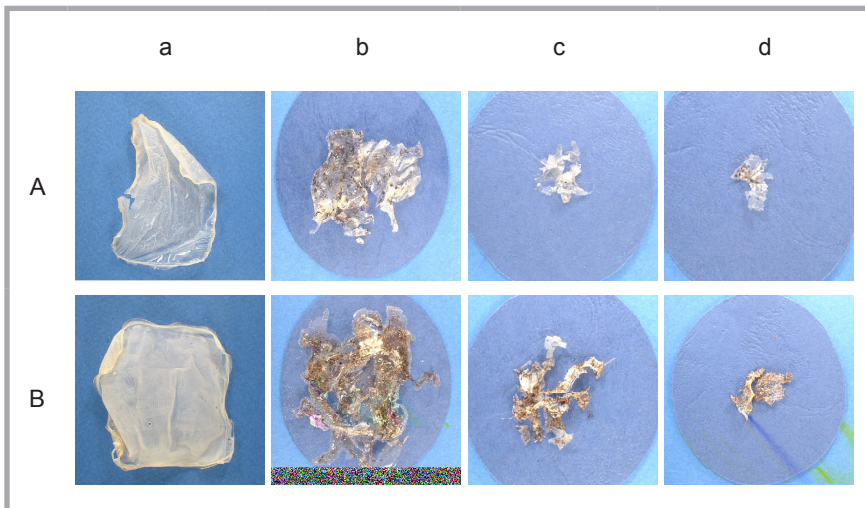
**Figure 4.** General appearance of chitosan lactate modified VS non-wovens differing in surface weight during biodecomposition in communal wastes.; a - initial VS non-woven with a surface weight of 20 g/m<sup>2</sup> (A) and 50 g/m<sup>2</sup> (B) modified by buffered chitosan lactate solution, b - after 2 weeks, c - after 4 weeks, d - after 6 weeks.



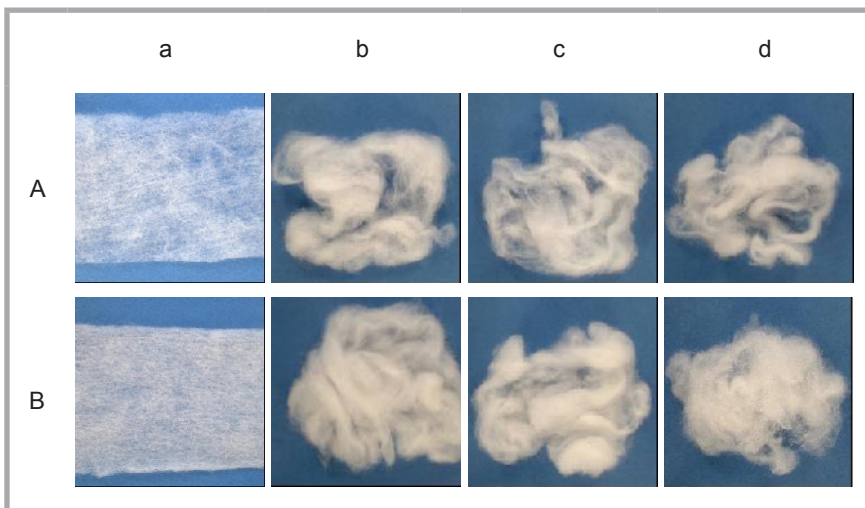
**Figure 5.** Results of soil test of films made of a solution of chitosan lactate buffered to pH = 5.4 with or without calcium; a - Initial film made of buffered chitosan lactate solution (A) and containing calcium (B), b - after 1 day, c - after 2 days, d - after 3 days.



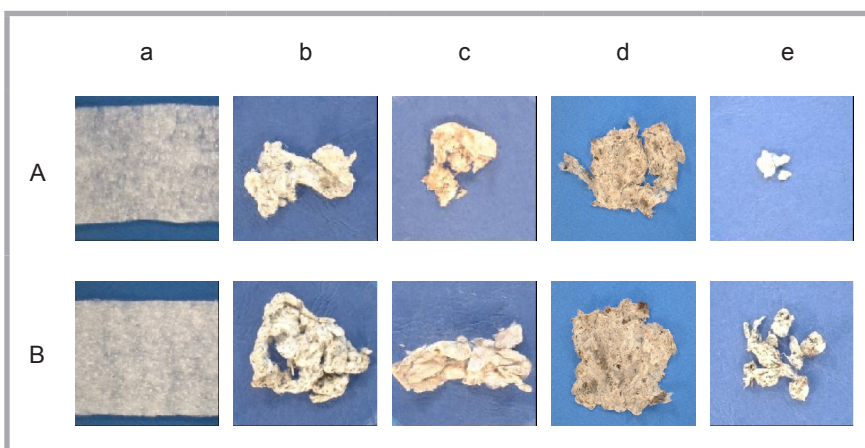
**Figure 6.** Results of soil test of films made of a solution of chitosan hydrochloride and chitosan acetate buffered to pH = 5.4; a - Initial film made of buffered chitosan hydrochloride (A) and acetate (B) solution, b - after 1 day, c - after 2 days, d - after 3 days.



**Figure 7.** Results of soil test of films made of a solution of chitosan hydrochloride and chitosan acetate both containing calcium and buffered to pH = 5.4; a - Initial film made of buffered chitosan hydrochloride (A) and chitosan acetate (B) solution containing calcium, b - after 1 day, c - after 2 days, d - after 3 days.



**Figure 8.** General appearance of chitosan lactate-modified PP non-wovens differing in surface weight after soil test degradation; a - initial PP non-woven with a surface weight of 20 g/m<sup>2</sup> (A) and 50 g/m<sup>2</sup> (B) modified by buffered chitosan lactate solution, b - after 1 month, c - after 2 months, d - after 3 months.



**Figure 9.** General appearance of chitosan lactate-modified VS non-wovens differing in surface weight after soil test degradation; a - initial VS non-woven with a surface weight of 20 g/m<sup>2</sup> (A) and 50 g/m<sup>2</sup> (B) modified by buffered chitosan lactate solution, b - after 3 weeks, c - after 5 weeks, d - after 6 weeks, e - after 8 weeks.

especially taking into account their biodegradability.

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