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Formation of Microfibres from Cellulose Acetate Butyrate by Electrospinning with a Surface Modified in Low-temperature Plasma

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Abstract
This work describes a method of formation of microfibres from cellulose acetate butyrate solution in acetone by electrospinning. The method used a specially designed electrospinning reactor with an arrangement generating low-temperature plasma incorporated in the spinning zone. In this study the low-temperature plasma treatment was used to modify the surface of cellulose acetate butyrate fibres. The chemical nature of the microfibres' surfaces was examined by UV-Vis spectroscopy with the use of an integration sphere and reflectance FTIR spectroscopy. Scanning electron microscopy (SEM) was used to determine the morphology and size of the electrospun fibres modified in low-temperature plasma and to compare them with the unmodified fibres.

Key words: *electrospinning, low- temperature plasma, processing reactor, microfibers, UV-Vis, spectroscopy, FTIR spectroscopy, SEM.*

Introduction

Electrospinning has been recognised as an efficient method for the fabrication of submicron-sized fibres. Classical electrospinning consists of using a high voltage electrical field applied between a needle capillary end and collector surface for drawing fibres, in the majority, from a solution or, more seldom, from a melt. An electrical charge is induced on a polymer solution deforming a spherical pendant droplet to a conical shape - the Taylor cone. The charged fluid jet is ejected from the tip of the cone and the solution is then elongated in the high-potential electrostatic field. Over this time the solvent evaporates from the solution. The fibres produced in this way may be collected on the opposite side of a metallic electrode or on the surface of an electrolyte [1 - 7]. The micro or nanofibres are made for different applications from medical dressing and implants to industrial products. One of them is the formation of filters [6]. In this application very important is the geometrical (morphological) and chemical structure of the fibre surface. One of the methods of chemical and physical modification in order to obtain special properties of the fibre surface is low-temperature plasma treatment [12 - 19]. This process is often used for an already finished product, especially a nonwoven consisting of microfibres.

The aim of our research was to obtain microfibres from cellulose acetale butyrate designed for filtering applications. Our problem to be solved was obtaining fibres of relatively small diameter with a developed surface from a material which is advantageous for filtering cigarette smoke and is easy degradable in a natural environment. It would be also advantageous to obtain fibres with the whole surface modified, which is rather difficult to obtain in a process modifying the web already formed after electrospinning. While planning the experiments, we considered that besides classical electrospinning devices, systems also exist which not only enable the formation of standard microfibres but also permit to realise additional functions [8 - 10]. It was assumed that a special reactor should be designed (***Figure 1***) which permits spinning microfibres from cellulose acetate butyrate solutions in acetone and simultaneously allows to modify the fibre surface. It was assumed that the low pressure in the inside space or the reactor, together with the high voltage of the basic process should create a low temperature plasma around the Taylor cone which would modify the surface of the newly formed microfibre around the whole circumference of the fibre, changing its morphology and producing an evidently new product.

The electrospinning reactor was designed as a universal electrospinning frame able to fulfil a series of different functions. However, a complete description of the numerous use possibilities of the device is not the subject of this article.

Experimental

Materials

- Cellulose acetate butyrate (CAB): – 29.5 wt.% acetyl and 17 wt.% butyryl content. Average M_n ca. 65,000, density 1.25 g/cm^3) purchased by Aldrich Co.Ltd., USA
- Acetone pure P.A. CAS No. 67-64-1 received from POCH Co. Ltd., Poland

Preparation of spinning solutions

Cellulose acetate butyrate (CAB) was dissolved in acetone at a concentration of 7.5 wt%. The solution was stirred vigorously at room temperature for at least 24 h in order to obtain a homogeneous mixture.

Characterisation of microfibres

- The morphology of microfibres was investigated by means of scanning electron microscopy. A JEOL JSM 5500 LV (Japan) scanning electron microscope was used operating in the backscattered electron mode at an accelerating voltage of 10 kV. The microfibres were sputtered with gold in a Jeol JFC 1200 ionic sputtering device. The observations of microfibres were performed at a magnification of 20,000 ×.
- The microfibres obtained were characterised by FTIR and UV-Vis spectroscopy. The spectroscopy investigations were carried out using a FTIR spectrophotometer 6700, made by Nicolet, USA, equipped with an 'Easy Diff' adapter, and by a spectrophotometer - Evolotion 600, made by Thermo Electron Corporation, USA equipped with an integrating sphere - DRA-EV-600.

Preparation of electrospinning

The electrospinning reactor designed consists of a multifunctional unit which enables working at a great range of different conditions applied during the process of electrospinning. For example, the following conditions can be applied: decreased or increased pressure in the coag-

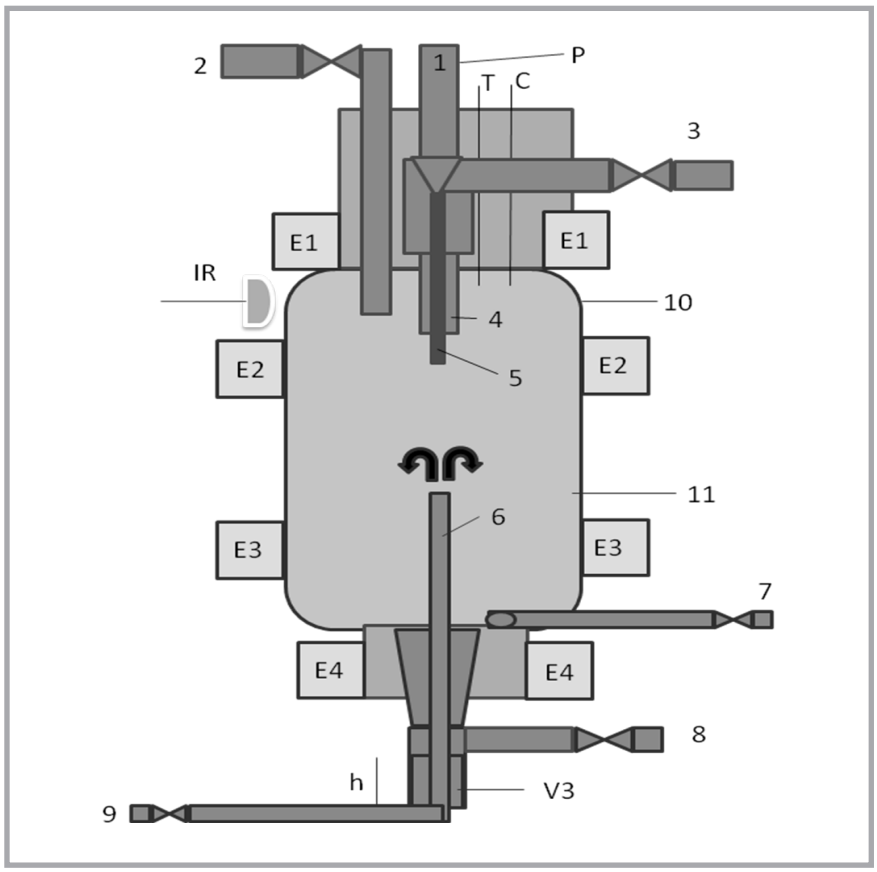

Figure 1. *Schematic diagram of the electrospinning reactor. 1 - spinning solution inlet, 2 - gas supply, 3 –supply of impulses of compressed gas, 4 - gas outlet with spinneret tube inside, 5 - spinneret (outlet for spinning solution), 6 - outlet for coagulation liquid or transporting microfibres, 7 - inlet for coagulation liquid or liquid transporting microfibres or for creating over-pressure/under-pressure during the process of continuous fibre production, 8 - outlet for transporting microfibres outside, 9 - supply of coagulation liquid or liquid transporting microfibres, 10 – part of the body of the reactor, 11 – part of the body of the reactor (pipe with flanges), P - connection for wires from a high-voltage generator, forming the first electrode, T - Temperature sensor, C - Pressure sensor (manometer), E1-4 - Electromagnetic coils, IR - Infrared radiator, h - Pipe in which a continuous stream of liquid produces under-pressure in the reactor and transports continuous fibres during their formation to the collecting system. The stream of liquid is the second electrode of the high-voltage source.*

ulation and solidification zones, various temperatures (by blowing in thermostated air or gases), an inert-gas atmosphere preventing the ignition of flammable solvents, application of vapours enabling coagulation with the use of toxic substances, and generation of glowing discharges enabling the use of plasma.

In this work an electrospinning reactor was used to obtain microfibres under low pressure, enabling the impact of low temperature plasma. A schematic drawing of the reactor is presented in ***Figure 1***.

Its elements and their functions are as follows:
1 - spinning solution inlet, 2 - gas supply, 3 - supply of impulses of compressed gas, 4 - gas outlet with spinneret tube inside, 5 - spinneret (outlet for the spinning solution), 6 - outlet for coagulation liquid or transporting microfibres, 7 - inlet for coagulation liquid or liquid transporting microfibres or for creating over-pressure/under-pressure during the process of continuous fibre production, 8 - outlet for transporting microfibres outside, 9 - supply of coagulation liquid or liquid transporting microfibres, 10 - part of the body of the reactor, 11 - part of the body of the reactor (pipe with flanges), P - connection for wires from a high-voltage generator, forming the first electrode, T - Temperature sensor, C - Pressure sensor (manometer), E1 - E4 - Electromagnetic coils, IR - Infrared radiator, h - Pipe in which a continuous stream of liquid produces under-pressure in the reactor and transports continuous fibres during their formation to the collecting system. The stream of liquid is the second electrode of the high-voltage source.

The electrospinning reactor is an entirely new device which does not have any equivalent even among other spinning reactors [18 - 20]. In order to investigate how it affects fibre formation and whether they could be used to modify fibre this way, an attempt at electrospinning was made using a spinning solution of 7.5% cellulose acetyl butyrate containing 29% acetyl groups and 17% butyrate groups in acetone. Reference samples were spun in the reactor maintaining the following parameters: pressure of 100 kPa, temperature of 19 °C, a solution extrusion rate of 10 cm^3/h, spinneret inside diameter of 0.25 mm, distance between the spinneret and opposite electrode (vertical water jet) 15 cm, temperature of coagulation water of 10 °C, and a voltage between electrodes of 60 kV. Spinning in low-temperature plasma was conducted under the same conditions as for the reference samples, with the pressure additionally reduced to 80 kPa and finally to 40 kPa. The lower pressure led to characteristic plasma glow in the vicinity of the electrode, visible in ***Figure 2***.

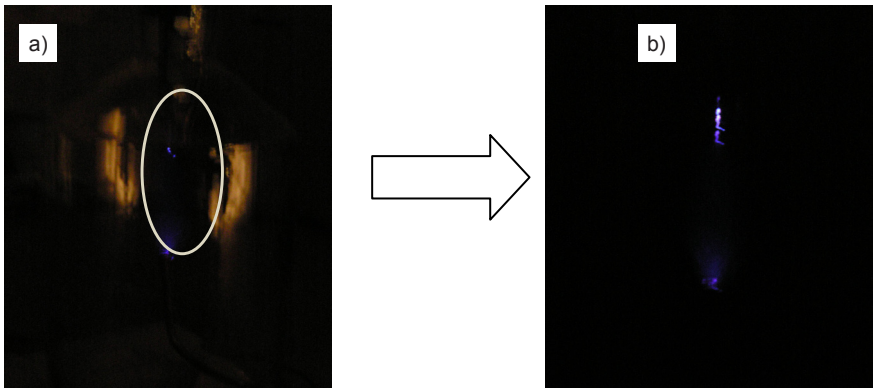

Figure 2. *Photographs of the inner space of the electrospinning reactor during electrospinning of cellulose acetyl butyrate fibres under pressure lowered to 40 kPa;* a) *– fragment of spinneret, b) – vicinity of electrode tips.*

The CAB spinning solution was poured into a feeding container and under pressure transported through the inlet (1) to

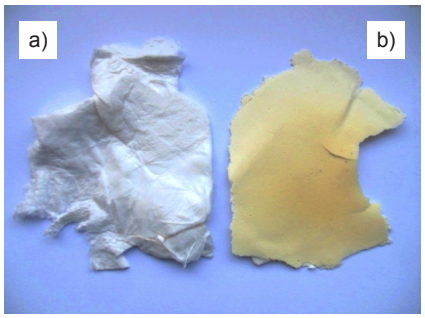

Figure 3. Photograph of webs obtained from cellulose acetyl butyrate: a – unmodified, and b – modified with low-temperature plasma at 40 kPa. The unmodified web is withered.

the spinning reactor. The solution flowed at a rate of 10 cm^3/h to the spinneret with a capillary of an outer diameter of 1 mm positioned centrally in the tube (4). Pipe (3) secures the injection of gas pulses under defined pressure enabling the breaking down of small polymer solution agglomerations from the outlet of the capillary (5) through the inlet (1) of the spinning solution. The high voltage supply wire (P) of negative polarisation is connected to the capillary (5). The gas supply inlet (2) is connected to a vacuum pump, which provides decreased pressure inside the reactor. Microfibres formed in the vicinity of the outlet of the capillary (5) are at the same time under the impact of the electrostatic field, causing their stretching and the action of the low temperature plasma modifying their surface. The plasma is visible as glowing blue in the surrounding of the capillary electrode, documented in the photographs in ***Figure 2***. The positive polarised electrode is formed by pipe (6), connected by wire (h) to a high voltage generator. The second electrode is formed by the liquid streams flowing through the outlet of pipe (6), marked by black curved arrows in ***Figure 1***. The liguid is supplied by pipe (9). The liquid (particularly water) takes the microfibres collected, spun from the capillary, and transports them to the bottom of the reactor, which is rinsed by the water supplied by pipe (7). The suspension of microfibres in water is transported outside the reactor by outlet (8). The fibres are deposited on a sieve in a closed container, which secures the tightness of the system. The water from the container is directly returned to collectors (7) and (9) with the use of a pump. Microfibres modified by the low temperature plasma are obtained in the form of a nonwoven deposited on the sieve. The electromagnetic coils (E1 - E4) serve to create magnetic fields which can be used for causing a special impact on electrically charged particles in the space of fibre formation. The use of these coils may be specially advantageous when microfibres are formed from solutions of good electrical conductivity. In the work presented herein, coils were not used.

Results and discussion

The area of the low-temperature plasma depends on the arrangement and shape of the upper electrode, and with its change, the area also varies. As the spinning solution emerges from the capillary and fibres are formed, the area has an elongated, narrow shape, roughly corresponding to that of the fibre formation space. Finally where the fibres settle on the vertical water jet above (6), their shape resembles a wide, blurred cone. The non-woven fabrics obtained are shown in ***Figure 3***.

The photo presents an unmodified fibre web as the smooth background (right), and the fibre web modified at the pressure decreased to 40 kPa with low-temperature plasma (left); the unmodified web seems to be wither.

Here should be emphasised that we did not achieve proper plasma modification until decreasing the pressure to 40 kPa. Decreasing the pressure to only 80 kPa does not give a satisfying effect.

The scanning microscope images (***Figure 4.a*** and ***4.b***) show that the lower pressure of 40 kPa applied with low-temperature plasma influenced the morphology of the fibre surface considerably.

The fibres visible in the photos have a diameter of even below 1 μm, whereas those modified by low-temperature plasma almost 2 μm

The fibres spun and modified at a pressure of 40 kPa are thicker and their surface highly corrugated. This effect could be achieved only due to the lowered pressure and the fact that it could be connected with faster acetone evaporation from the spinning solution during fibre formations.

In order to check the impact of low-temperature plasma on physic-chemical changes in the structure of surface layers of the microfibres obtained, tests were performed using UV-Vis and FT-IR spectroscopy.

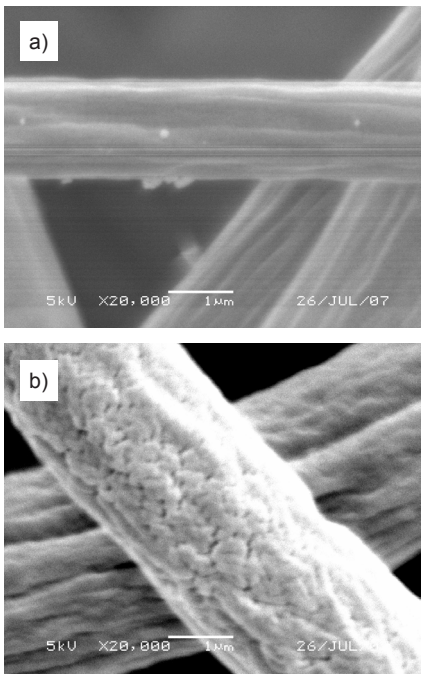

Figure 4. SEM Photographs - images of fibres obtained from cellulose acetyl butyrate: a) under normal conditions, b) modified in low-temperature plasma at 40 kPa.

Figure 5 (see page 40) presents UV-Vis spectra of micro-fibre samples obtained with the use of an integrating sphere, obtained for a series of microfibre samples spun in the electrospinning reactor under pressure conditions of 100 kPa (atmospheric pressure) and decreased pressure of 80 kPa and 40 kPa. The decrease in pressure in the internal space of the reactor caused a more intensive impact of the plasma on the surface of the fibres leaving the spinning capillary. This effect is visible in the form of an increase in the intensity of the maximum of the band in the range of about 300 nm. The absorption of short waves in the visible range has its effect in a yellowish shade, which can be explained by the influence of C=0 groups.

The changes observed in the UV-Vis spectra clearly show the influence of fibre oxidation. Strong absorption growth at about 320 nm results in the fibres becoming yellow, which is probably due to the forming of C=O groups.

Figure 6 (see page 40) presents a comparison of FT-IR reflection of non woven samples obtained in the electrospinning reactor at atmospheric pressure and decreased down to 40 kPa with the simultaneous action of low temperature plasma. specially attained with the use of a Nicolet 6700 spectrofotometer equipped with

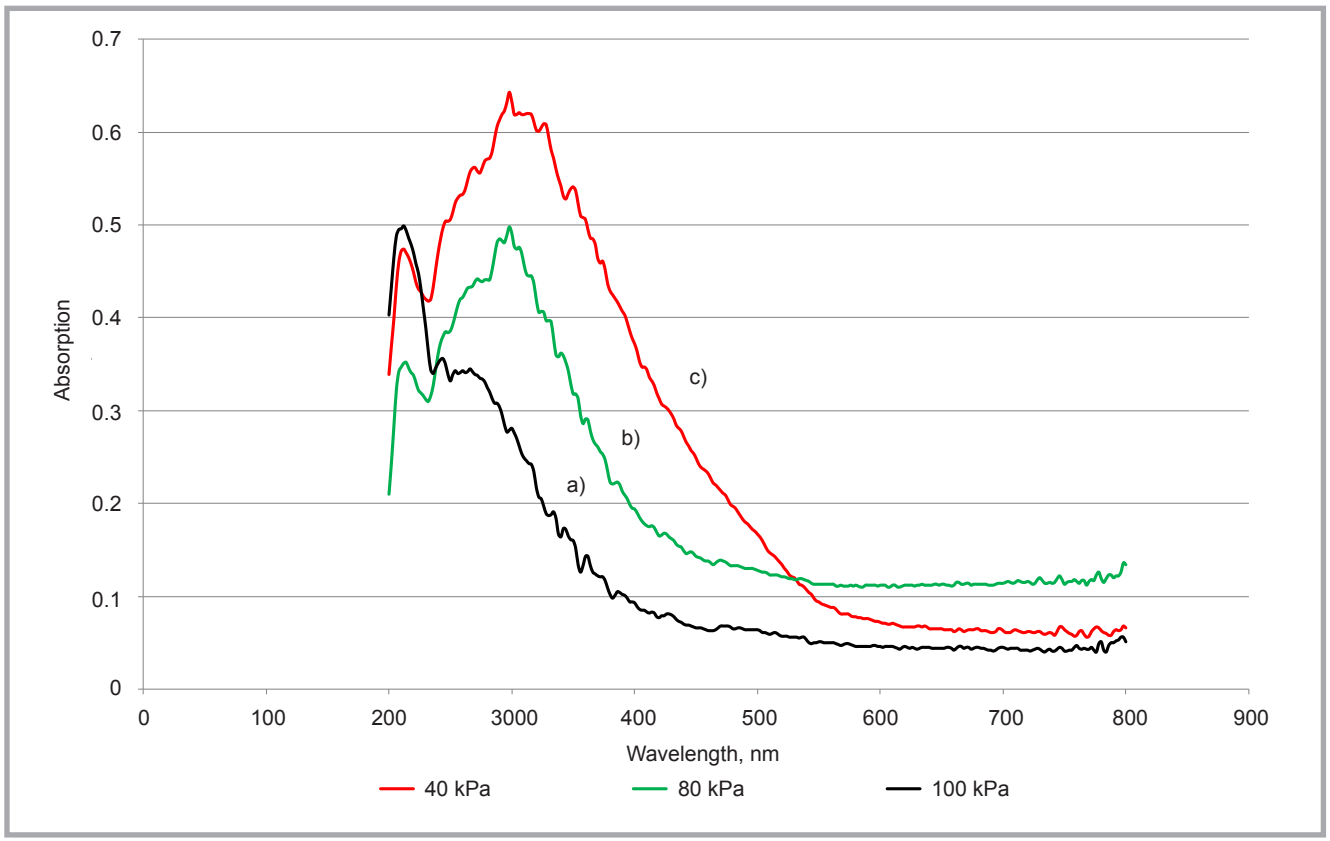

Figure 5. *Comparison of UV-Vis spectra obtained with the use of an integrating sphere of microfibre samples from a series both unmodified and affected by low-temperature plasma in the electrospinning reactor: a) 100 kPa – atmospheric pressure, b) pressure lowered to 80 kPa, c) pressure lowered to 40 kPa.*

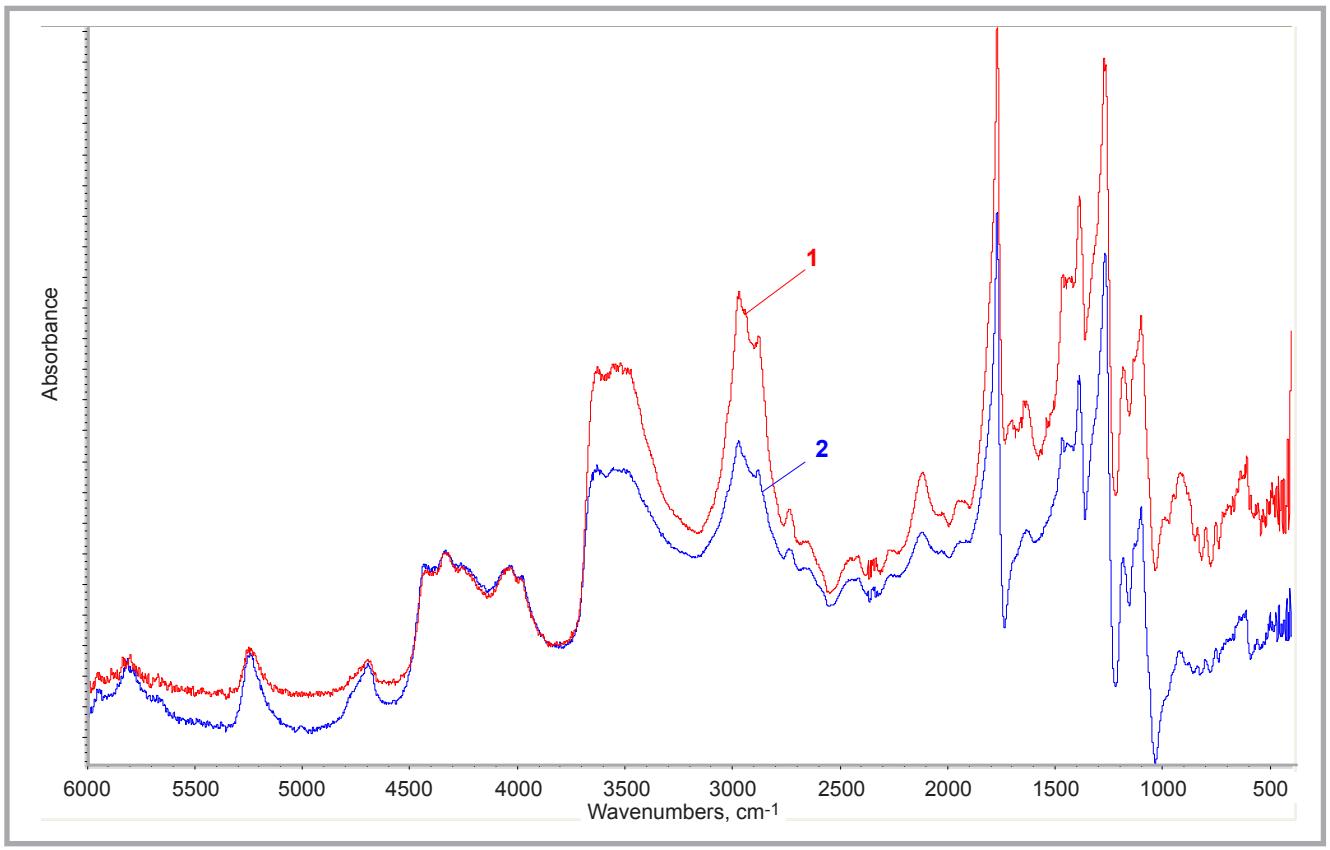

Figure 6. *Comparison of FT-IR reflection spectra within the range of 6000 - 500 cm^{-1} obtained from non-wovens of unmodified fibres and those subjected to low-temperature plasma at 40 kPa and at 1 - spectra of non-wovens subjected to low-temperature plasma at 40 kPa; 2 - spectra of non-woven fabrics subjected to atmospheric pressure.*

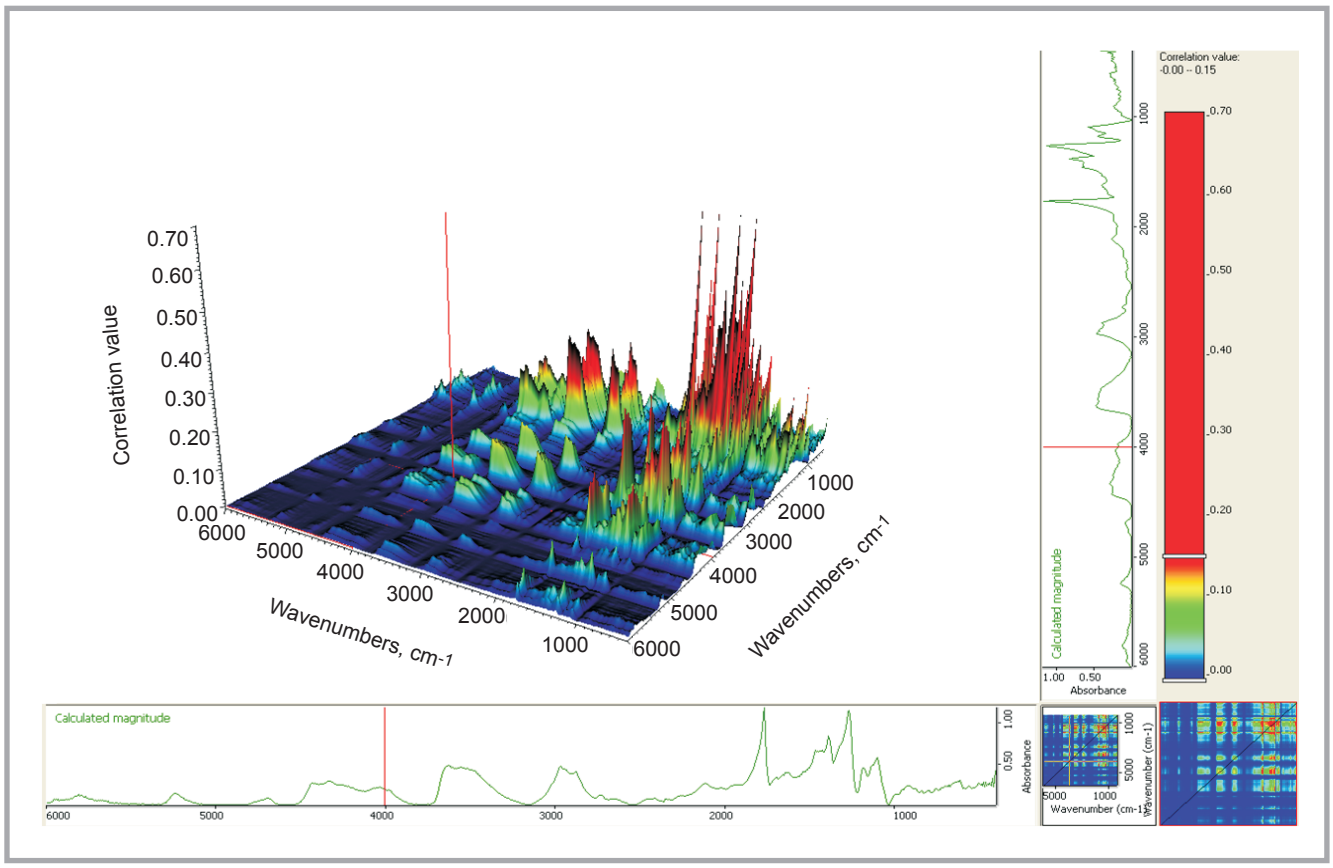

Figure 7. *Synchronous two-dimensional correlation of the spectra in the 6000 - 400 cm^{-1} range for non-woven samples treated with low-temperature plasma in the area of fibre formation.*

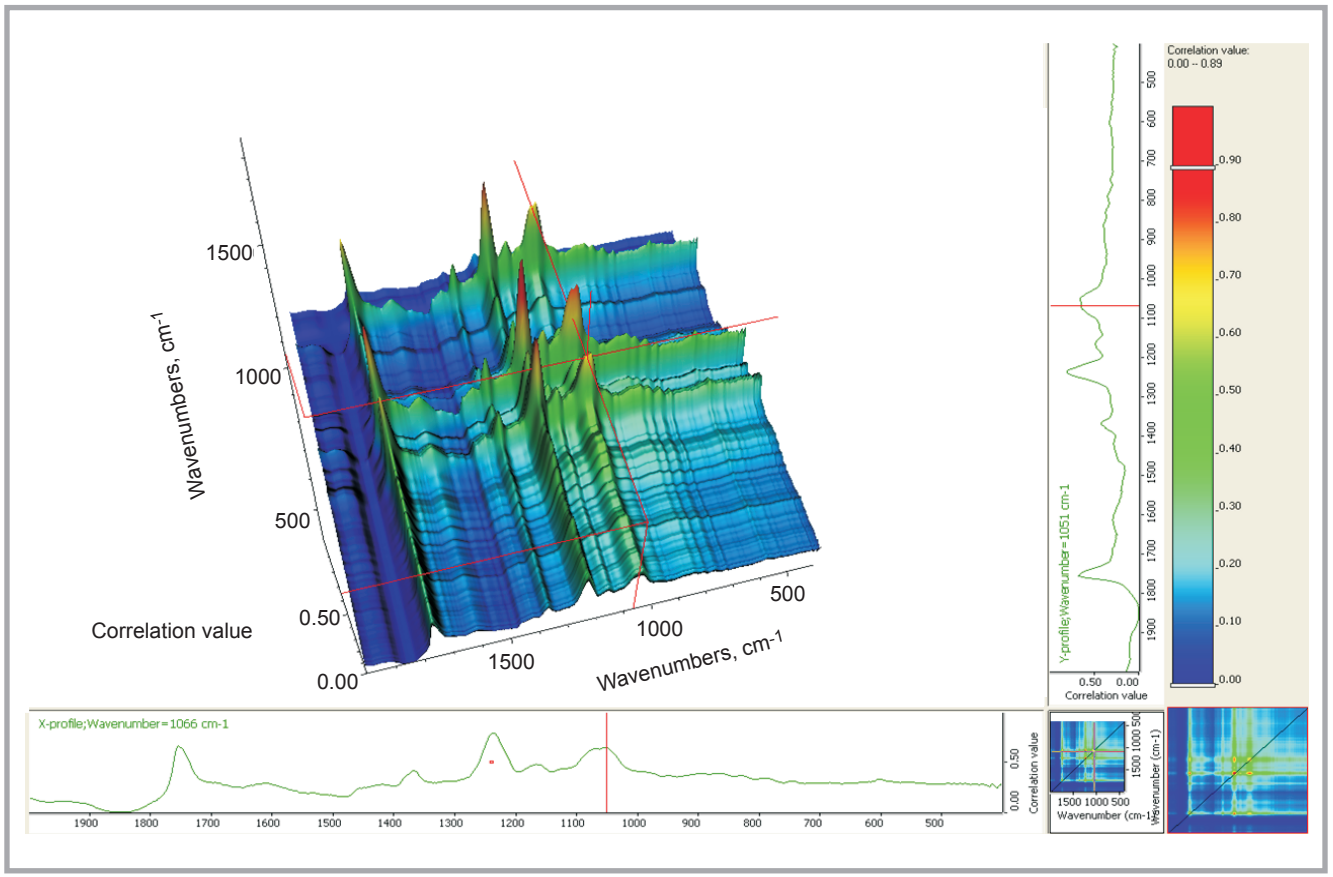

Figure 8. *Synchronous two-dimensional correlation of the spectra in the 2000 - 400 cm^{-1} range for non-woven samples treated with low-temperature plasma in the area of fibre formation.*

a reflectance adapter - "Easy Diff". The whole spectra do not differ generally, but a significant change can be observed within the range of about 1,000 cm^{-1}, where absorption bands of configurations characteristic for carbon-oxygen bolds are visible. The increase in intensity of these bands confirm that low-temperature plasma causes oxidation of the micro-fibres modified.

The spectra obtained do not reveal any substantial changes in the chemical structure of the nonwovens. After applying the Kramers-Kronic relation to anomalous reflection below 2,000 cm^{-1}, and after another phase of quantitative normalisation of the band 2965 cm^{-1}, these spectra were compared using a synchronous two-dimensional correlation. The synchronous two-dimensional correlation of the spectra within the range of 6,000 - 400 cm^{-1} are presented in ***Figure 7*** (see page 41) and for the range within 200 - 400 cm^{-1} in ***Figure 8***.

Differences in the spectra between samples spun in the reactor under conditions of atmospheric pressure and decreased pressure with the simultaneous impact of low-temperature plasma are shown in ***Figures 7*** and ***8***. The majority are within the spectrum range characteristic for structures containing oxygen, visible in the form of a group of sharp peaks in the range of 1400 - 900 cm^{-1}. Changes in the chemical structure of the samples caused by low-temperature plasma are also visible in the range of 2,900 cm^{-1}, probably caused by the decrease in the number of C-H bonds, as well as in the range of about 3,400 cm^{-1} , caused by O-H groups appearing and their influence through hydrogen bonds.

As can be seen, chemical groups are formed, whose oscillations produce absorption bands in the range of wave numbers characteristic for C-O and C=O bond S. This means that the surface of the microfibres is strongly oxidised, one visual effect of that being the yellowish hue of the nonwovens

Conclusions

It was confirmed that the electrospinning reactor designed and constructed by us was useful not only for successfully obtaining microfibres of cellulose acetate butyrate, but it also gives us the possibility to modify the surface of fibres obtained by low-temperature plasma. We could obtain fibres with a porous surface layer and with a chemically altered structure around the whole circumference. It can be assumed that the new fibres used in filters should have better filtration properties.

The new electrospinning reactor makes it possible to modify the surface of the freshly spun fibres. However, the product is obtained in the form of a web, finally individually forming a nonwoven.

Acknowledgement

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