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Nanofiber Sheets with the Superabsorbent Properties

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Abstract: The new electrospinning technology Nanospider^{TM} offering a realistic potential for industrial production was used for creation of nanofiber sheets from aqueous solutions of partially neutralized poly(acrylic) acid with crosslinking agent. Produced nanofiber sheet was crosslinked by heat treatment. Absorption capacity and rate of absorption were tested and compared with superabsorbent particles and commercial superabsorbent fibers. The morphology of electrospun fibers was observed using a scanning electron microscope (SEM). Possibilities of fiber diameter influence were studied.

Introduction

The need for commodity stuff produced by nonwoven technologies containing nanofibers continues to increase. The diameters of nanofibers are generally understood to be less than about 1000 nanometer (one micron). Nanofibers webs are desired due to their high surface area, low pore size, and other advantageous characteristics. The nanofibers, also commonly called microfibers, can be produced by a variety of methods and from a variety of materials, e.g. by modified melt blown technology [1,2,3] or by film fibrillation method [4]. Although several methods have been used, there are drawbacks to each of the methods and production of cost effective nanofibers has been difficult. Therefore, hygiene articles and other disposable consumer products containing nanofibers have not been marketed.

Today, superabsorbent polymers (SAPs) are manufactured in form of fine granules or powder with a broad particle size distribution. From the absorption point of view, small particles are preferred, because of their higher absorption speed due to higher specific surface. Larger sizes provide lower absorption speed. On the contrary, larger granules can be better anchored in the wood pulp structure and do not tend to escape as dust outside of the absorption sheet. High tendency of small particles for migration is limiting the total amount of SAP that can be used.

Superabsorbent polymers (SAPs) are loosely crossslinked networks that can absorb a large amount of water in a short time and retain water under the pressure. Therefore, SAPs have great advantages to traditional water-absorbing materials as cotton, pulp, sponge, etc. SAPs are widely used in sanitary goods such as disposable diapers and hygienic napkins. They are also valuable in some specialized applications, such as agriculture [5], horticulture [6], dew-prevention coating [7], sealing composites in long-distance cable [8], firefighting [9] and drug delivery [10,11].

The most common superabsorbent polymers used in the hygienic industry are based on poly(acrylic) acid (PAA). The degree of neutralization is one of the important characteristics of the final product jointly with the molecular mass, being usually between 100.000 and 250.000 g/mol. Cross-linked PAA provides a strong thickening effect by forming aqueous gels and in dried form it possesses a high water absorption capacity (more then 100 g/g). Such products are known as superabsorbent polymers.

By using SAP nanofibers, made by the new electrospinning continual process [12,14], due to their network structure with a micro- or nano-thickness of typically less than1-2 μm, any migration of SAP could be fully avoided for of high portion of SAP in absorption core almost unlimited by danger of migration. Thereby the electrospinning process can be performed in a way, which would easily allow including a nanofiber sheet to the manufacturing of absorption sheets.

Materials and Methods

Superabsorbent polymers

Two swelling pastes (i) W 103335 and (ii) W 101524 (Stockhausen,Germany) were tested for electrospinning. They contained water solution of polyacrylic acid (PAA) with 50% degree of neutralization in sodium salt. Molecular mass of PAA was (i) 120.000 g/mol and (ii) 220.000 g/mol. Polyethylenoxid with molecular mass 300 g/mol was used as crosslinking agent. Electrospun concentrations of pastes were (i) 44% wt. and 38% wt. (W 103335) and (ii) 28%wt. (W 101524).

Electrospinning of SAP fibers

Electrospinning of polymers was performed on a laboratory model of Nanospider technology device. The scheme of the device is shown in Fig. 1 and it was described in detail previously [12]. This is a completely original method of production of fibers in the diameter range tens of nanometers to tens of micrometers. On the thin layer of polymer solution film (2, Fig. 1) raised by a metal roller (1), which is at the same time positive electrode, the so-called Taylor cones are formed due to the effect of high voltage (20-70 kV). The cones cleave into fibers, which are carried onto the negative electrode (6) and caught by a polypropylene non-woven fabric (4). During the process, the solvent evaporates and the fibres stretch at laboratory or elevated temperatures.

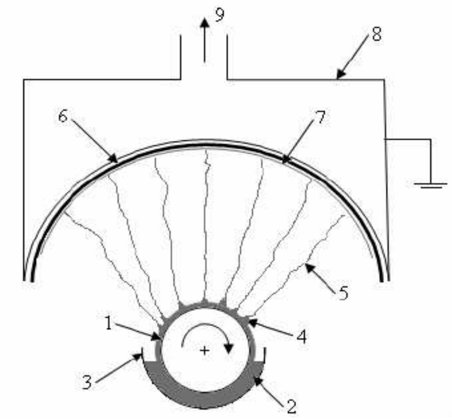


Fig. 1: Principle of electrospinning.
1 – metal roller as positive electrode,
2 – fiber - forming polymer layer,
3 – reservoir of polymer solution,
4 – textile substrate (supportive material),
5 - fiber formation direction,
6 – electrode earthing shield,
7 – air suction

The reservoir (3) was filled with 20 ml of polymer solution; rotation of the cylinder ensured its perfect coating. A regulable high-voltage power supply, which can produce voltage ranging from 0 to 55 kV, was used for electrospinning (Glassman High Voltage, Inc., USA). Electric field was switched on and successively increased until an optimum course of electrospinning was reached. Optimum value of electrostatic field is different for every polymer solution. If the optimum value of electrostatic voltage was known, it was set up already at the beginning of the process. Formation of optimum Taylor cones and hence also optimum electrospinning process was achieved by setting up the rotational speed of the cylinder. Electrospinning of PAA solution was carried out on a laboratory continual model of Nanospider technology device [12] by high voltage from 50 kV to 58 kV and by 0,1 m distance of electrodes, air temperature 22 ºC and air humidity 35%.

Processed nanofiber sheets were crosslinked by heat treatment (190ºC / 7 min).

Morphological and physical properties of submicron fibers

The morphology of the electrospun fibers was observed using a scanning electron microscope (SEM). The fiber diameter was measured by commercial software from the scanning electron micrographs in original magnification of 10^4 x. Computer with software Lucia G was used for fiber diameter evaluation. Test data were statistically processed used Microsoft Excel, version 7.0.

Absorption capacity was tested after slightly modified EDANA standard (10.1-72) by using 0,9 %wt. natrium chloride. Typically, the SAP (about 0,2 g) was immersed in 100 g distilled water in a 250 ml beaker flask with a closing plug and allowed to soak for time 60 s at 25 ºC. The swollen gel was then separated from unabsorbed water by screening through a 120 -mesh sieve and allowed to drain for 120 s. The sieve was then weighed to determine the weight of swollen gel. The absorbency (Q) was calculated using the following equitation:

$$Q = (W_2 - W_1) / W_1 \tag{1}$$

where W_2 and W_1 are the weights of the swollen gel and the dry resin, respectively.
Q was calculated as mass of water (g) per mass of dry polymer (g).

Method for determination of the absorption rate index

Slightly modified ARI testing method was used [11]. A 100 ml graduated cylinder was filled of 0,9 wt % aqueous solution. Superabsorbent polymer sample having particles in the range of 250 to 650 micrometer was used. The portion of 1,00 g of the screened polymer was dumped into the graduated cylinder. When the sample first reached the bottom of the cylinder, a timer accurate to the nearest second is started. The volume of the gel layer is measured in defined time sequences for 480 min. The data is plotted and the time required for the volume of gel to reach 60% of its maximal value at 8 hour is determined by interpolation. This time is reported as the t_{60} time. The gel volume was compared for SAP particles and SAP sheets at the 3 min time.

Results and Discussions

Many parameters can influence the transformation of polymer solution into nanofibers through electrospinning. These parameters include (a) the solution properties, such as viscosity, conductivity and surface tension, (b) governing variables such as electric potential between electrodes, distance between roller and collecting screen and (c) ambient parameters such as temperature, humidity and air velocity at suction in the electrospinning chamber. It was found and confirmed that concentration of polymer solution could influence not only the electrospinning process but fiber diameters also.

We focused on processing SAP nanofibers with the lowest fiber diameter. It was found that the easier way is reducing of polymer concentration in the electrospun solution. We also compared an effect of molecular weigh of two types of polyacrylic acid used in SAP.

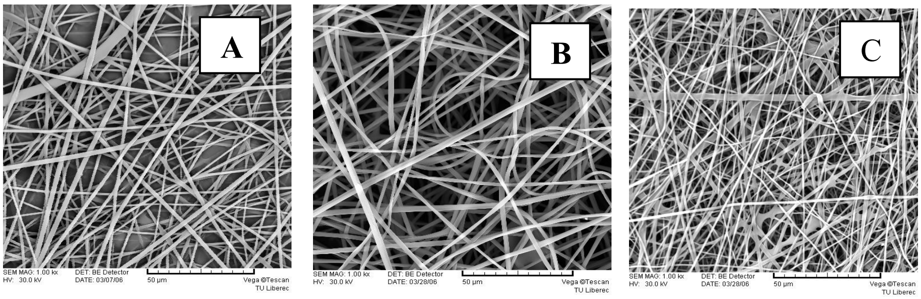


Fig.2: SEM micrographs of the nanofibers before wetting made from swelling paste W 103335 (A,B) and W 101524 (C) with various concentra-tions: 1A: c=38% wt., 1B: c=44% wt., 1C: c=28%wt.,(original magnification 1 000x).

Sorption capacity of SAP depends also on the surface area of fibers or particles. When the fiber diameter decreases, then specific surface of fibers increases.

Specific surface (P_{spec}) of nanofibers was expressed from equitation (2) for mean fiber diameter

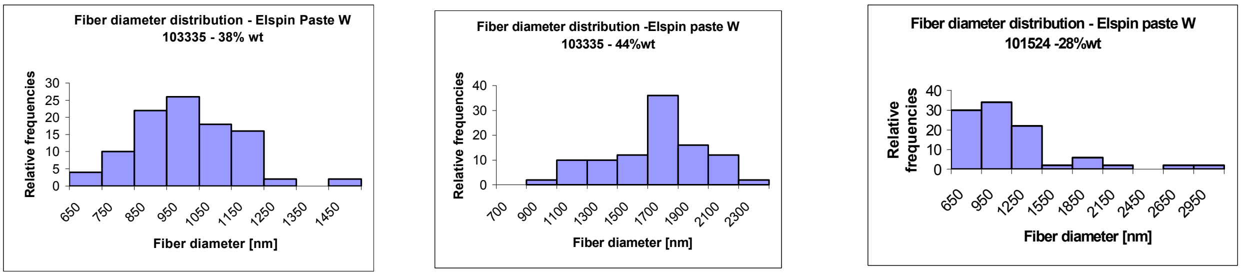
$$P_{spec} = P / M = (\pi D .L) / (\pi . D^2 /4 . L .\rho) \tag{2}$$

Where P is surface area of nanofibers [m^{-2}], M is mass [kg], D is average fiber diameter [m], L is length of fibers [m] and ρ is polymer density [$kg.m^{-3}$]. After equitation adapting is possible to write

$$P_{spec} = 4 / (D\,.\rho) \tag{3}$$

The calculated values are in the Table 1.

Fiber diameters were evaluated from SEM micrographs of nanofiber sheets, mean fibers diameter was assessed and according equation (3) specific surface of fibers was calculated. Gained values were compared with specific surface commercial processed superabsorbent fiber OASIS SAF^{TM} diameter 30 μm , density 1,4 g/cm^3.



A B C

Fig.3: Histograms of fiber diameter made from swelling paste W 103335 (A,B) and W101524 (C) with various concentrations: 1A: c = 38% wt., 1B: c = 44% wt. 1C:c = 28% wt.

Histograms in the Fig.3 show obviously, that the concentration of polymer solution influences the fiber diameter. Optimal spinable concentration ranges in this case from 38 to 44 %wt (paste W103335) and 28 %wt (paste W 101524). Electrospinning of polymer solution of lower concentration then 28 % results in beads formation.

Sorption capacity of nanofiber web was tested in 0,9 % natrium chloride with very good results, so supper absorbent material should accept more then 30 g of testing solution per 1 g of dry polymer. Stability of nanofiber sheets after water treatment (distilled water / 22ºC, 2 hours) was confirmed by using SEM micrographs. Structure of nanofibers is persistent enough after water treatment and could be used for water absorption repeatedly (Fig.4). Fiber morphology has remained almost unchanged during swelling and during following drying of these sheets (Fig.4).

Absorption capacity was controlled by time of crosslinking reaction and it changed from full solubility of nanofiber sheets to a negligible swelling only. Optimal heat treatment was assessed by 190ºC during 7 min, which leaded to results mentioned in Table 1.

Table 1: Specific surface of processed nanofibers versus fiber diameter and sorption capacity

Type of fiber	Average fiber diameter [µm]	Specific surface [m^2/g]	Absorption capacity [g/g]	Volume of gel [ml/3 min]	Variation coefficient of absorption capacity [%]
Fibers OASIS 102	30	0,095	25	non-measurable	---
Nanofiber– W 103335 (concentration 44%)	1,65	2,05	28,13	95 ?	26,44
Nanofiber – W 103335 (concentration 38%)	0,96	3,53	30,81	77 ?	10,12
Nanofibers – W101524 (concentration 28%)	1,11	3,05	28,84	80 ?	14,42
SAP particles	250-650	-	24,7	43	---

Although it is known [9] that sorption properties of commercially processed staple fibers Oasis (Technical Absorbent Ltd) are on the level about 25 g/g, these fibers could be processed only as a fiber blend with contents of SAP fibers maximally 50 % wt. Oasis fibers changed to the formless mass after wetting. Very good sorption capacity of OASIS fibers with low specific surface could be explained by lower crosslinking density that corresponds well with loss of their shape after dipping into a liquid.

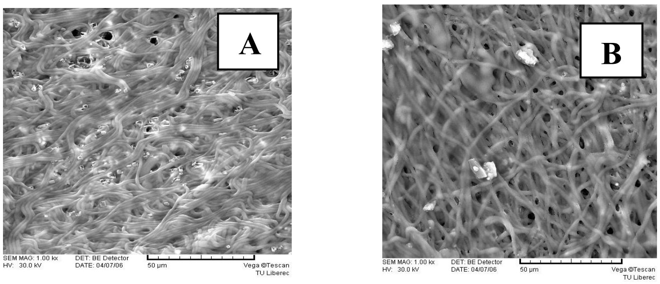


Fig. 4: SEM micrographs fiber sheets made from the paste W 103335 (A) and W 101524 (B) over swelling in the distilled water and following drying

Conclusions

- Superabsorbent submicrone fiber sheets based on partly neutralized PAA were prepared by continual elecrospinning process and crosslinked by heat treatment.
- Fiber diameter was evaluated from SEM micrographs, the histograms were constructed and a specific surface area of fibers was calculated as 2 - 3 m^2 / g.
- Weight areas of processed submicrone sheets were between 1 and 2 g/m^2, fiber diameters were from 650 to 2300 nm.
- Optimal concentration of electrospun polymer solution was found for given molecular mass of poly(acrylic) acid, the value of molecular mass influences the electrospinning process and fiber diameters.

- Sorption capacity was measured and compared with commercial processed superabsorbent fiber OASIS 102 and commercial SAP particles of defined diameter. SAP nanofiber sheets have a slightly higher absorption capacity compared to SAP particles and commercial fibers but rate of their absorption is expressively higher thanks to specific surface of nanofibers.
- ARI Test Methods is not fully suitable for evaluation of nanofiber sheets because of immediate swelling and insufficient sedimentation of small pieces of SAP sheets.

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