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"Surface modification of polypropylene nonwoven substrates by padding with antistatic agents for deposition of polyvinyl alcohol (PVA) nanofiber webs by electrospinning"

Abstract

In the last years, the electrospinning process has become one of the most interesting processes to obtain nanofiber webs with interesting properties for uses in a wide variety of industrial sectors such as filtration, chemical barrier, medical devices... as a consequence of the relatively high surface/volume ratio. Among the wide variety of polymers, polyvinyl alcohol (PVA) offers good advantages since it is water-soluble and this fact enables easy processing by electrospinning. There are many variables and parameters to be considered in order to optimize PVA nanofiber webs: some of them are related to the polymer solution, some others are related to process and some of them are related to the collector substrate. In this work a study on the effects of two different surface pre-treatments on a nonwoven polypropylene substrate as collector of PVA nanofiber webs has been carried out. In particular, a chemical treatment with anionic antistatics and a physical treatment with low pressure plasma have been investigated. The effects of these pre-treatments on morphology of PVA nanofiber webs have been followed by SEM. Results show that surface resistivity is one of the main parameters influencing the web formation as well as the nature of the electric charge achieved by the pre-treatment. The plasma treatment promotes changes in surface resistivity but it is not enough for good web deposition. Chemical pre-treatment (padding) with anionic antistatic leads to a decrease in surface resistivity up to values in the $1 \cdot 10^{09} - 1 \cdot 10^{11}$ Ω which is enough for good nanofiber deposition.

Keywords: surface modification; fiber, yarn, fabric formation; chemical modification; spinning

1. Introduction

In the last decade, electrospinning has become one of the most versatile techniques to obtain nanofibers at both laboratory and industrial scale. Nanofibers offer great possibilities in a wide variety of industrial sectors. It is important to remark their use as high efficiency filters and chemical barriers (with potential uses in medical devices, pharmacy and even in army applications and other technological uses as those of automotive, aeronautics and aerospace) [1-10]. Furthermore, the use of nanofibers in biomedicine (tissue engineering) is increasing in a remarkable way since some nanofibers could be compatible with human body and also could allow cells attachment and proliferation; so that, they can be useful for bandages and/or scaffolds for tissue and bone regeneration [11-14]. On other hand, nanofiber webs are also used for drug controlled release due to their porous nature [15-19].

Polyvinyl alcohol (PVA) is one of the most interesting polymers for nanofibers' obtaining. Its water-soluble nature is an important factor for easy processing by the electrospinning process [20, 21]. It shows high resistance to chemicals and in many cases it offers biocompatibility and biodegradability. All these properties, together with easy processing, makes PVA one the most interesting polymers for nanofibers' production at industrial level.

The obtaining of PVA nanofiber webs from a PVA solution by the electrospinning process has been widely investigated in the last years. Due to its water-soluble nature, it is relatively easy to obtain PVA nanofibers in comparison to other polymer systems. The electrospinning process with PVA can be carried out at

environmental conditions (the relative humidity must be maintained in the 30-50% range) thus avoiding fitting-out systems. Despite this, there are many variables that can influence the overall final performance of the nanofiber webs, mainly related to average size and statistical distribution. The main parameters are related to three items: polymer solution, electrospinning equipment and its processing parameters, and finally, collector substrate nature [22-28].

Regarding the polymer solution, it is important to remark the role of the molecular weight, surface tension and conductivity [29-31]. The average molecular weight and its statistical distribution determine the system rheology and as a consequence, many processing parameters such as voltage, current intensity... are derived from solution rheology. With regard to surface tension, it is important to remark that charges in the polymer solution must be high enough to overcome the solution surface tension. Also, we have to take into account that the electrospinning process is highly related to charge repulsion that appears in the solution surface. As the solution conductivity increases, the ability to form electrical charges increases and thus, thin polymer fibres can be obtained [32]. In the case of PVA, the pH affects in a remarkable way and optimum results in terms of nanofibers' size and uniformity are obtained for extreme pH values [33].

On other hand, the electrospinning equipment plays an important roll. Concerning the process parameters, it is important to note the role of the applied voltage intensity which is directly related to solution nature [34]. As the voltage increases, the nanofiber diameter decreases; this fact can lead to presence of internal stresses that promote changes in crystallinity. Furthermore, crystallinity can be influenced by some additives and several web post-treatments [35]. It is also important to remark the importance of the distance between the electrodes. It is necessary a minimum threshold

distance to ensure complete solvent (water in the case of PVA nanofibers) evaporation. Once this threshold has been reached, an increase in the distance can lead to a decrease in the nanofiber diameter but it is important to take into account that there is also a maximum threshold distance; if this is exceeded, the electrical field between the two electrodes is broken and then, nanofibers stop flowing [36].

With regard to the collector substrate, it is important to note that it must be capable to maintain the electrical field between the charged solution (which is in direct contact with an electrode) and the opposite electrode which is located just behind the collector substrate. With respect to textile substrates it is advisable to work with thin, small thickness and small surface density textiles. In most cases, nonwoven structures satisfy all these requirements. The role of the textile collector is to act as a support for nanofiber web deposition and contribute to the overall resistance of the composite structure. Also, the presence of the textile collector enables easy handling of nanofibers' webs.

The aim of this work was to carry out a study on the effects of a surface pre-treatment on a nonwoven polypropylene as collector substrate for polyvinyl alcohol (PVA) nanofiber webs obtained by electrospinning process. The nonwoven substrate was subjected to two different pre-treatments: the first one, a physical treatment by low pressure plasma with O_2+CH_4 mixture gas and the second one a chemical process (padding) with anionic antistatic agents. Once the surface pre-treatments were completed, the electrospinning process was carried out and the effects of these two pre-treatments on nanofibers' formation and webs' morphology were investigated by SEM analysis.

2.- Experimental

2.1.- Materials

We have worked with a polyvinyl alcohol water solution Sloviol®R (Novacke Chemicke Zavody, a.s., Novaky, Slovak Republic) which is obtained by alkaline hydrolysis of polyvinyl acetate in ethanol. The molecular weight of PVA was 67000 g mol^{-1}. Table 1 summarizes the main characteristics of the PVA water solution.

Table 1

The precursor solution for nanofiber webs formation was prepared by diluting the appropriate amount of Sloviol®R with water quality type II to obtain a final PVA concentration of 14 weight %. The total amount of solution prepared for the electrospinning process was 250 cm^3; after that 1.7 cm^3 of phosphoric acid (Mallinckrodt Baker B.V., Deventer, Netherlands), 75 weight % with a purity of 85%, with a molecular weight of 98 g mol^{-1} and a density of 1.685 g cm^{-3}, were added to modify solution conductivity.

As a reference collector substrate for nanofibers' deposition, a polypropylene 100% nonwoven spunbond commercial grade Pegatex®S (Pegas Nonwovens, s.r.o., Znojmo, Czech Republic) was selected. This is characterized by a surface density of 16.5 g m^{-2} and it is provided with an antistatic finishing to enhance nanofiber deposition. Its surface resistivity is $3.81 \cdot 10^{11}$ Ω and the vertical resistivity is $2.78 \cdot 10^{11}$ Ω.

As a sample collector substrate (untreated), a commercial grade polypropylene 100% nonwoven spunbond Vicatex® (Vicatex NV, Ontinyent, Spain) with a surface density of 30 g m^{-2} was selected. Surface resistivity of this substrate is around $3.96 \cdot 10^{15}$ Ω and the vertical resistivity is $2.00 \cdot 10^{14}$ Ω.

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2.2.- Electrospinning process

The electrospinning process was carried out in a laboratory equipment Nanospider[TM] NS-Lab supplied by Elmarco (Elmarco s.r.o., Liberec – Ruzodol, Czech Republic). This equipment is provided with two electrodes between which a high voltage discharge is generated; the bottom electrode is a spinning stainless steel cylinder (drum) which is partially submerged in a tray with the PVA polymeric solution; so that, the cylinder drags a thin layer of the polymer solution in each spin (see Figure 1[a]). On the other hand, the collector electrode is located in the upper zone of the apparatus and it is in full contact with the textile substrate which glides in a continuous way between the two electrodes. The electrospinning box is sealed while the equipment is running and an air current is generated to maintain the appropriate airing.

The electrospinning process is conducted as follows: the bottom electrode (drum) rotates at a constant rate. In each spin, it drags a small amount of the PVA solution (depending on the viscosity); when the electrical forces at the surface of the small layer of PVA solution dragged by the drum are high enough, then it is possible to overcome surface tension and it is possible to form a charged jet that is ejected from the cylinder drum. As the solvent evaporates, a charged nanofiber is formed. This is directed to the collector substrate by electrical forces to form a web.

The electrospinning process was carried out at a temperature of 24.8 ºC and a relative humidity of 42%. As this procedure is quite different to the typical needle process, one of the main control parameters is the collector substrate speed which determines the surface density of the deposited PVA nanofiber web. In this research, the collector substrate speed has been set as constant for all trials at 12.50 Hz or 0.325 m

min^{-1}.A summary of the main parameters used for nanofiber deposition is shown in Table 2.

Figure 1

Table 2

2.3.- Surface treatments of PP collector substrate

Two surface treatments were used to modify surface properties of the polypropylene collector substrate Vicatex®: a chemical treatment with anionic antistatics and a physical treatment with low pressure plasma.

The chemical treatment was used to modify surface resistivity and an anionic antistatic commercial grade P-552 supplied by Colorcenter (Colorcenter S.A., Terrassa, Spain) was used for the padding process. This antistatic is a fatty acid derivative with a pH of 9 (solution of 10%) and a density of 1.03 g cm^{-3}; the appropriate concentration of this antistatic for the padding is 15-20 g L^{-1}. This range was selected to provide the appropriate surface resistivity for nanofiber deposition. Figure 2 shows the FTIR spectrum with the main peaks and bands regarding this antistatic. As we can see, typical absorption peaks/bands of fatty acids and derivatives (mainly esters) are detected in the 1467 cm^{-1}- 978 cm^{-1} range [37]. Figure 3 shows the main thermal transitions of the antistatic with a crystallization/melting peak located at -3.1 ºC.

Figure 2

Figure 3

The physical process used to modify polypropylene substrate was low pressure glow discharge plasma (LPGDP). The collector substrates were exposed to radio frequency (RF) low pressure glow discharge plasma with a methane-oxygen mixture gas. It was used a glow discharge RF generator (operating at 13.56 MHz) type CD 400 MC option PC (Europlasma, Oudenaarde, Belgium). The gas used for the plasma generation was a mixture of CH_4-O_2 with a volume ratio 80:20. It was used a gas flow rate of 100 cm^3 min^{-1} and the working pressure was maintained around 42 Pa. The working power was fixed to 152 W and the exposure time to cold plasma was set to 5 min.

2.4.- Experimental techniques

Characterization of thermal transitions of the anionic antistatic was carried out by differential scanning calorimetry (DSC) with a Mettler-Toledo 821 (Mettler-Toledo Inc., Schwerzenbach, Switzerland). All tests were conducted in nitrogen atmosphere (30 mL min^{-1}). Sample material was subjected to a cooling program from 30 ºC to -60 ºC at a cooling rate of -5 ºC min^{-1}; after that a heating ramp from -60 to 25 at 5 ºC min^{-1} was conducted.

Infrared analysis of the anionic antistatic was performed on a BRUKER - Tensor 27 Standard System equipped with attenuated total reflexion (ATR) accessory. 32 scans with a resolution of 4 cm^{-1} were carried in the 4000-600 cm^{-1} wavenumber range.

Changes in surface wettability of modified substrates were determined by contact angle measurements. Static contact angles of the collector substrates were measured at room temperature on a KSV CAM 200 goniometer (KSV Instruments, Helsinki, Finland) using water and diiodomethane as test liquids. At least six different measurements were obtained and the average values for contact angles were calculated.

Surface and vertical resistivity of the collector substrates were measured following the guidelines of the UNE EN 1149-1:2007 and UNE EN 1149-2:1998 respectively. The tests were carried out in a Eltex equipment Tera–Ohm–meter 6206 (SDL Atlas, Textile Testing Solutions).

The laminar mass or surface density was determined by cutting 100 cm^2 samples with a circular die (James H. Heal & co. Ltd, Halifax, England) and weight measurements were carried out in a precision balance Mettler Toledo, mod. AE240 (Mettler-Toledo Inc., Schwerzenbach, Switzerland).

Morphology of the nanofiber webs was investigated with a scanning electron microscope FEI Quanta 200 (FEI Company, Oregon, USA) in order to characterize nanofiber diameter and web's homogeneity. Prior to observation, samples were coated with a sputter coater POLARON mod. SC7620 (Quorum Technologies, East Sussex, England) and a rotative vane vacuum pump Edwards RV5 with gas filtering. The average diameter of nanofibers was determined using the image analysis software supplied with the microscope, XT Docu (Analysis Image Processing).

3. Results and discussion

3.1. Characterization of PVA nanofiber webs on polypropylene nonwoven substrates without previous treatment

As we have described before, there are a lot of variables that take part in the formation of nanofiber webs by the electrospinning process. In addition to some variables related to the polymer solution (concentration, additives…) and the electrospinning control parameters (voltage, distance between electrodes, current intensity…) the characteristics of the collector substrate could restrict in a great extent formation of optimum webs since it can contribute to attraction or repulsion of the

obtained nanofibers. An appropriate surface finishing will contribute to a correct deposition of nanofibers from the PVA water solution. On the other hand, some surface treatments could lead to partial deposition of webs (due to repulsion forces which produces nanofibers' dispersion) and, subsequently, poor web quality. In most cases, the original collector substrate requires a surface pre-treatment to provide surface charges in order to obtain good quality webs. Figure 4 shows a SEM microphotograph of the polypropylene nonwoven spunbond collector without nanofibers. We can clearly observe the typical structure of the spunbond with fibre sizes in the micro-scale range. As the spunbond is a well controlled process, fiber dispersion is tight as seen in Figure 4 (between 14 and 16 µm).

Figure 4

Figure 5 shows several SEM microphotographs (with different magnification) of a PVA nanofiber web deposited onto a polypropylene nonwoven spunbond without any surface pre-treatment. For low magnification (Figure 5[a]), the web fully covers the collector substrate and it appears to be a correct deposition process. Nevertheless, for higher magnification we can observe in a clear way the structure of a heterogeneous web obtained without any pre-treatment. In Figure 5b (600x), we can clearly distinguish polypropylene fibers coming from the collector substrate partially covered by a heterogeneous PVA nanofiber web; we can see great amount of circular formations (holes) which contribute to heterogeneity. The same structure can be seen for higher magnification (1200x, Figure 5[c]); also we can observe presence of small PVA webs but they are irregularly dispersed. Figure 5(d) (2400x) clearly shows an irregular deposition of PVA nanofibers on the collector substrate; really, we can observe these

partial PVA webs but it is clearly distinguishable presence of PVA agglutination which covers some polypropylene fibres and, obviously, do not form nanofibers. This could be related to the fact that the solvent has not evaporated prior to nanofiber deposition and as a consequences, this has a negative effect on the overall appearance of the PVA web; this fact has a negative effect on the overall appearance of the PVA web as described by other authors [35, 38]. So we can conclude that deposition of nanofibers occurs but the nature of the untreated polypropylene collector substrate leads to irregular deposition so that the nanofiber web efficiency is dramatically decreased since it is impossible to obtain the maximum surface/volume ratio.

Figure 5

3.2. Effect of surface treatment and finishing of nonwoven polypropylene substrates on nanofiber webs morphology

With the aim of improving PVA nanofibers' deposition and subsequent webs' homogeneity, we have proceeded with two different surface treatments that are easy to transfer to industrial scale: a chemical treatment (padding) with antistatic agents and a physical treatment with low pressure glow discharge plasma with O_2+CH_4 mixture gas [39, 40].

The low pressure glow discharge plasma (LPGDP) treatment with O_2+CH_4 mixture gas leads to a remarkable increase in surface wettability of the collector substrate due to surface functionalization and roughness increase by deposition of a nanometric plasmapolymerized organic layer [39]. This wettability improvement can be detected by studying the variation of contact angle between the polypropylene substrate and a test liquid; so that, the water contact angle is reduced from a initial value of 110.9º

(untreated polypropylene) up to values of 84.7º with an exposure time of 5 min. Regarding diiodomethane as test liquid, the initial contact angle (63.3º) is reduced up to 57.4º. These results show a noticeable increase in surface wettability; despite this, this wettability improvement do not favours deposition of PVA nanofibers as we can corroborate in Figure 6. Our previous results with LPGDP with O_2+CH_4 mixture gas on polypropylene substrates show a remarkable increase in surface oxidation ratio (O/C) ratio so functionalization is one of the main plasma-acting mechanisms and contributes to presence of active moieties (mainly oxygen based species). This fact has a positive effect on presence of electrical charges on plasma treated surfaces. Furthermore, an increase in weight is detected which is attributed to plasmapolymerization (deposition) of an oxidized-organic layer [41, 42]. As nanofibers are not appropriately collected onto the non-woven PP substrate, it is possible to think that the overall charge provided by the plasmapolymerization process does not favours nanofiber deposition in a great extent and many of them are repulsed. This is corroborated by changes in electrical properties of the plasma-treated substrate. Surface resistivity of the untreated polypropylene substrate is $3.96 \cdot 10^{15}$ Ω. The plasma treatment leads to a decrease in surface resistivity up to values of $5.05 \cdot 10^{13}$ Ω. This fact should favors deposition of PVA nanofibers but due to the nature of the plasmapolymerized layer, great amount of unstable polar groups are formed and this could lead to nanofibers' repulsion due to the intensity and nature of the electrical charges; subsequently, formation of homogeneous webs is not possible.

Figure 6

Previously to chemical treatment, we have evaluated the quality of the nanofiber webs deposited onto the reference polypropylene nonwoven substrate, Pegatex®S (supplied with antistatic surface finishing) and the overall results are remarkably better. The effects of this surface finishing on wettability properties are not significative (small contact angle variation for both water and diiodomethane). The initial water contact angle changes from 110.9º to 113.1º for the untreated and the chemically modified polypropylene respectively and diiodomethane contact angle changes from 63.3º (untreated) up to 66.1º (with antistatic surface finishing). Although this surface finishing does not produce important changes in wettability, surface resistivity is remarkably reduced. The initial surface resistivity of the untreated polypropylene ($3.96 \cdot 10^{15}$ Ω) is reduced up to values of $3.81 \cdot 10^{11}$ Ω, and this represents a decrease of about 4 order of magnitude. This decrease enables deposition of PVA nanofibers on the collector substrate due to the nature of the electrical charges. So it is important to remark the role of the surface resistivity and presence of electrical charges as two of the main control parameters to obtain good quality webs. Figure 7 shows different SEM microphotographs of PVA nanofiber webs deposited onto the reference polypropylene substrate (Pegatex®S) supplied with antistatic finishing. For low magnification (80x), the nanofiber web (Figure 7[a]) fully covers the surface of the collector substrate and this represents good homogeneity although some irregular fibres (higher diameter) can be detected as well as in Figure 7(b) with higher magnification (600x). Figure 7(c) shows a higher magnification (2400x) of the nanofiber web and we can clearly observe a homogeneous web with fibers sizing in the nano-scale range (in fact, it is possible to distinguish the polypropylene fibers below the PVA thin web with sizes in the micro-scale range). For higher magnification (5000x, Figure 7[d]) we also observe good homogeneity although, as described before, some thicker fibers can be detected.

Nevertheless, the overall homogeneity of the PVA nanofiber web is appropriate and we can conclude that the antistatic finishing promotes good deposition of PVA nanofibers thus leading to good quality webs.

Figure 7

3.3. Effects of the anionic antistatic concentration on overall morphology of PVA nanofiber webs

As we have described previously, surface resistivity together with nature of the electrical charges seem to be important parameters regarding the collector substrate for good nanofibres' deposition. Pegatex®S is a commercial grade with antistatic finishing and as we have seen, it shows a low surface resistivity that promotes good deposition of PVA nanofibers. From an industrial point of view, it is important to deeply know the characteristics of the surface finishing to evaluate its effects on the overall morphology of the deposited nanofibers. For this reason, surface finishing of polypropylene substrate (without any surface treatment, Vicatex®) with different concentrations of an anionic antistatic agent has been carried out by a padding process Table 3 shows the electrical properties of the collector substrate subjected to surface finishing with anionic antistatic agents with different concentrations ranging from 15.0 to 22.5 g L^{-1}. We can clearly observe a decrease in both surface and vertical resistivity as the concentration of the anionic antistatic increases.

Table 3

This reduction gives surface resistivity values similar to those observed for the reference polypropylene substrate (Pegatex®S). Figure 8 shows SEM microphotographs

of PVA nanofiber webs deposited onto polypropylene substrates with a chemical pre-treatment (padding) with anionic antistatic agents at different concentrations. Figure 8(a) shows the SEM microphotograph of a PVA web deposited onto a polypropylene substrate with a chemical pre-treatment with 15.0 g L^{-1} of anionic antistatic agent by padding; we see quite good homogeneity and uniformity. Nevertheless, we can observe presence of PVA agglutination in some areas. As the anionic antistatic agent concentration increases up to 17.5 g L^{-1}, we observe higher homogeneity and these material agglutinations are not detected so we could expect higher web efficiency. For concentrations of 22.0 and 22.5 g L^{-1}, PVA nanofiber webs show a fully homogeneous net structure and this is representative for optimum deposition of PVA nanofibers; on other hand, PVA agglutinations do not appear and this leads to optimum surface efficiency of PVA webs since the surface/volume ratio is remarkably increased. It is important to remark that nanofibers bear an electric charge (electrostatic charge) after electrospinning (this phenomenon is also used in filtration applications to improve efficiency) [43, 44]. As we can observe in Figure 8, deposition of PVA nanofibers is good so it is expectable that PVA nanofibers are positively charged after formation, so that, they are attracted by the collector substrate (with anionic antistatic finishing).

Figure 8

As we have described before in a qualitative way through Figure 8 observation, as the antistatic concentration increases, distribution and homogeneity of PVC deposited nanofibers improves in a significant way. On other hand, we have observed presence of PVA agglutination for low antistatic concentration. In a quantitative way, we can also characterize these processes. Table 4 shows the variation of the laminar mass or surface

density and the average nanofiber diameter in terms of the anionic antistatic concentration. Results regarding untreated polypropylene are not showed since nanofiber distribution is not homogeneous and a great amount of nanofibers are not deposited onto the collector substrate (they are repulsed). Concerning to nanofibers' sizes (without taking into account the formation of PVA agglutinations) we can see that the average diameter does not change in a significant way and it remains in the 270-290 nm range. This fact is representative for high efficiency of the electrospinning process. Nevertheless, with regard to the surface density, a clear tendency can be detected. The surface density changes from 52.63 g m^{-2} for the lowest concentration in this study (15.0 g L^{-1}) up to values of 37.23 g m^{-2} for an antistatic concentration of 22.5 g L^{-1} for the chemical pre-treatment by padding. These results are in agreement with those described in a qualitative way since presence of PVA agglutinations favours a increase in deposited PVA (bulk material); so that, the decrease in surface density could be representative for an improvement on web homogeneity while the fibre dimensions do not depend in a great extent on the anionic antistatic concentration used for the padding process.

Table 4

4. Conclusions

The electrospinning process is governed by a high amount of variables (process control, polymer solution as nanofiber precursor and collector substrate). With regard to the collector substrate, this study has revealed the need to reach certain surface properties in order to obtain good quality and homogeneous nanofiber webs.

Polypropylene nonwoven spunbonds without any surface pre-treatments are not appropriate collector substrates since deposited PVA nanofiber webs are not homogeneous and are characterized by the presence of many holes. This study has revealed that surface resistivity and nature of the electrical charges are two main parameters to be taken into account with regard to the collector substrate. The initial surface resistivity of the untreated polypropylene collector substrate is around $3.96 \cdot 10^{15}$ Ω. The addition of an anionic antistatic agent by a chemical treatment (padding) decreases surface resistivity to a range comprised between $1 \cdot 10^{09}$ and $1 \cdot 10^{11}$ Ω. Furthermore, negative charges are provided with the padding process. In these conditions, deposition of PVA nanofibers occurs in an appropriate way and a high quality PVA web with nanofibers sizing between 270-290 nm is obtained. On other hand, it is important to remark that the anionic antistatic concentration for the padding process has an important effect on the overall web morphology. Thus, in the range of concentrations used in this work (from 15.0 g L^{-1} to 22.5 g L^{-1}), as the concentration increases, we can observe an improvement on the web homogeneity and uniformity and also, PVA agglutinations practically disappear.

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Table captions

Table 1.- Characteristics of the polyvinyl alcohol (PVA) water solution used as precursor of nanofibers in the electrospinning process.

Table 2.- Summary of the control parameters of the electrospinning process used for deposition of PVA nanofiber webs on a polypropylene nonwoven collector substrate.

Table 3.- Variation of the electrical properties of the polypropylene nonwoven collector substrate in terms of the anionic antistatic concentration used for the padding process.

Table 4.- Variation of properties of the deposited PVA nanofiber webs on a polypropylene nonwoven collector substrate in terms of the anionic antistatic concentration used for the padding process.

Figure legends

Figure 1.- Representation of the Nanospider^TM electrospinning equipment, a) schematic representation, b) photograph of the Nanospider TM apparatus.

Figure 2.- FTIR spectrum of the anionic antistatic P-552 supplied by Colorcenter based on a fatty acid derivative.

Figure 3.- DSC graph of the anionic antistatic P-552 supplied by Colorcenter based on a fatty acid derivative, with the main transitions.

Figure 4.- SEM microphotograph (80x) of the polypropylene nonwoven substrate collector as received without any surface treatment.

Figure 5.- SEM microphotographs of a PVA nanofiber web deposited onto a polypropylene nonwoven substrate collector without any surface treatment at different magnification, a) 160x ,b) 600x , c) 1200x and d) 2400x.

Figure 6.- SEM microphotographs of a PVA nanofiber web deposited onto a polypropylene nonwoven substrate collector with a physical pre-treatment with low pressure plasma using O_2+CH_4 mixture gas, at different magnifications, a) 200x, b) 800x.

Figure 7.- SEM microphotographs of a PVA nanofiber web deposited onto a polypropylene nonwoven substrate collector modified with an antistatic surface finishing, at different magnifications, a) 80x, b) 600x, c) 2400x y d) 5000x.

Figure 8.- SEM microphotographs of a PVA nanofiber web deposited onto a polypropylene nonwoven substrate collector chemically modified by padding with different anionic antistatic concentrations, a) 15.0 g L^{-1}, b) 17.5 g L^{-1}, c) 20.0 g L^{-1}y d) 22.5 g L^{-1}.

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Table 1

Dry substance	% weight	16 ± 1.5
Solution viscosity (at 4%)	cps	9 - 13
Maximum acidity	mg KOH g^{-1}	4.5
Maximum specific conductivity	μS cm^{-1}	350

Table 2

Voltage (kV)	50.50
Current intensity (mA)	0.130
Electrode speed (rpm)	5.2
Substrate speed (Hz) / (m min^{-1})	12.50 / 0.325
Distance between electrodes (cm)	11

Table 3

Concentration (g L^{-1})	Surface resistivity (Ω)	Vertical resistivity (Ω)
0.0	$3.96 \cdot 10^{15}$	$2.00 \cdot 10^{14}$
15.0	$3.99 \cdot 10^{11}$	$1.63 \cdot 10^{09}$
17.5	$2.79 \cdot 10^{10}$	$5.97 \cdot 10^{08}$
20.0	$2.24 \cdot 10^{10}$	$5.08 \cdot 10^{08}$
22.5	$2.45 \cdot 10^{09}$	$7.01 \cdot 10^{07}$

Table 4

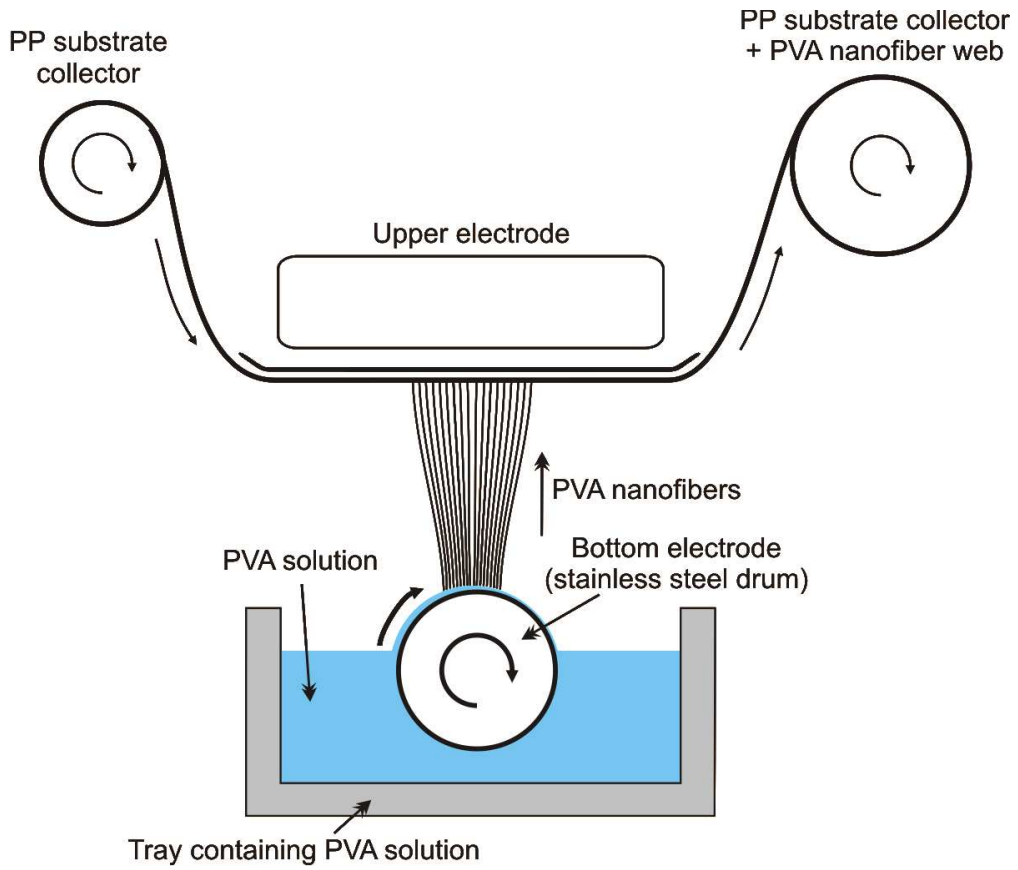| Concentration (g L^{-1})	Surface density (g m^{-2})	Average diameter size (nm)
15.0	52.63	287
17.5	46.18	285
20.0	42.32	277
22.5	37.23	291

Figure 1.- Representation of the NanospiderTM electrospinning equipment, a) schematic representation, b) photograph of the Nanospider TM apparatus.
101x86mm (300 x 300 DPI)

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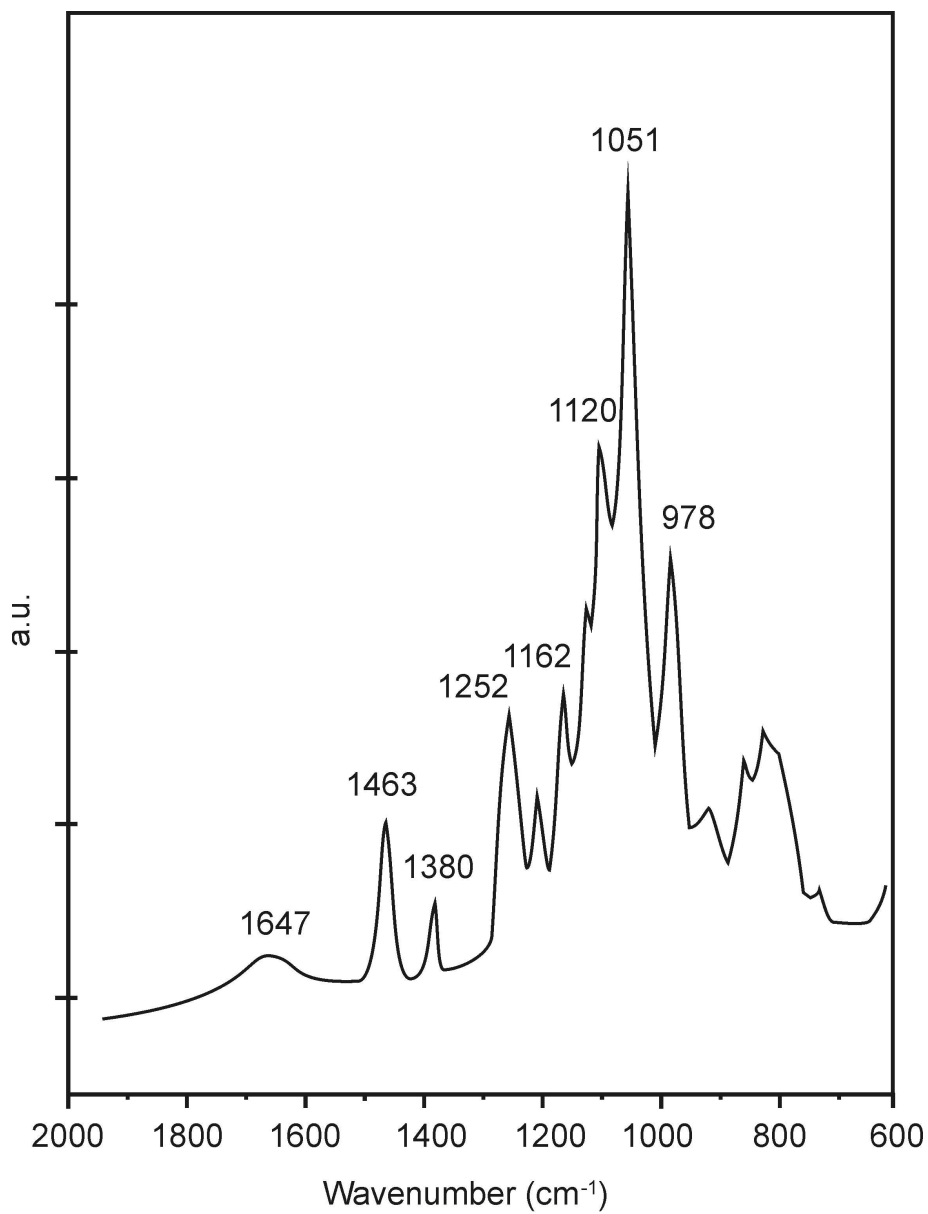43
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Figure 1.- Representation of the NanospiderTM electrospinning equipment, a) schematic
representation, b) photograph of the Nanospider TM apparatus.
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Figure 2.- FTIR spectrum of the anionic antistatic P-552 supplied by Colorcenter based on a fatty acid derivative.
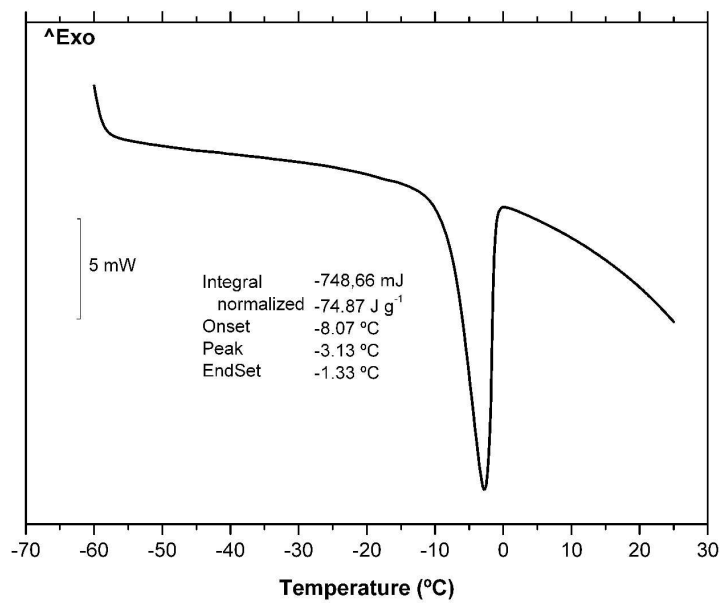98x129mm (600 x 600 DPI)

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Figure 3.- DSC graph of the anionic antistatic P-552 supplied by Colorcenter based on a fatty acid derivative, with the main transitions.
297x207mm (600 x 600 DPI)

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| 9/28/2006 | Mag | Det | Sig | Spot | HV | WD | 1.0mm |
| 2:21:56 PM | 80x | ETD | SE | 6.0 | 15.0 kV | 10.4 mm | |

Figure 4.- SEM microphotograph (80x) of the polypropylene nonwoven substrate collector as received without any surface treatment.
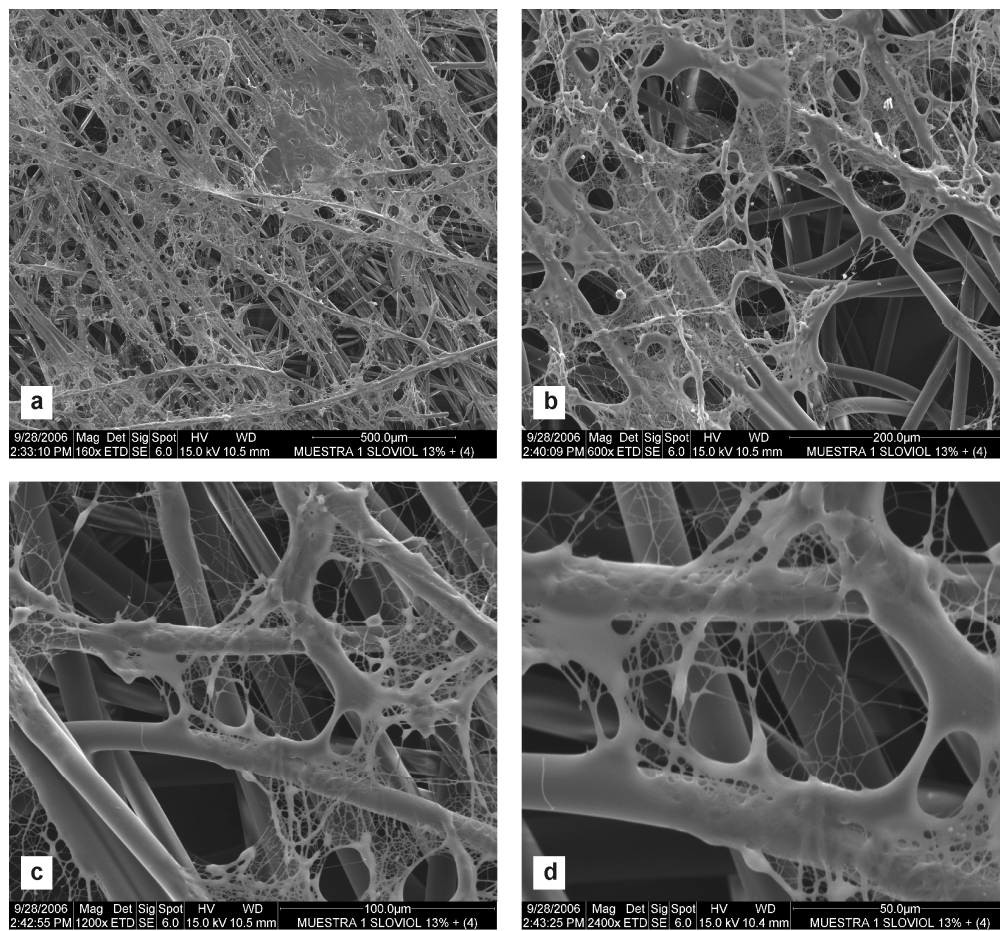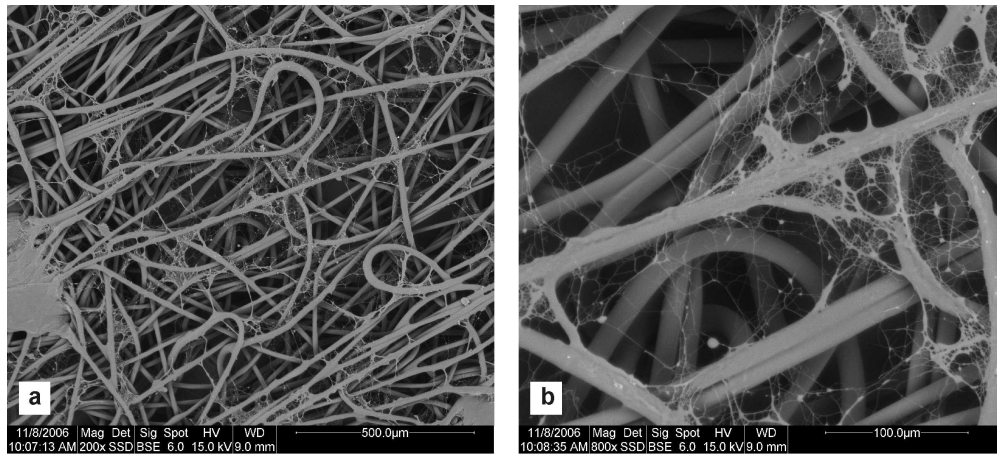541x499mm (96 x 96 DPI)

Figure 5.- SEM microphotographs of a PVA nanofiber web deposited onto a polypropylene nonwoven substrate collector without any surface treatment at different magnification, a) 160x ,b) 600x , c) 1200x and d) 2400x.

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Figure 6.- SEM microphotographs of a PVA nanofiber web deposited onto a polypropylene nonwoven substrate collector with a physical pre-treatment with low pressure plasma using O2+CH4 mixture gas, at different magnifications, a) 200x, b) 800x.
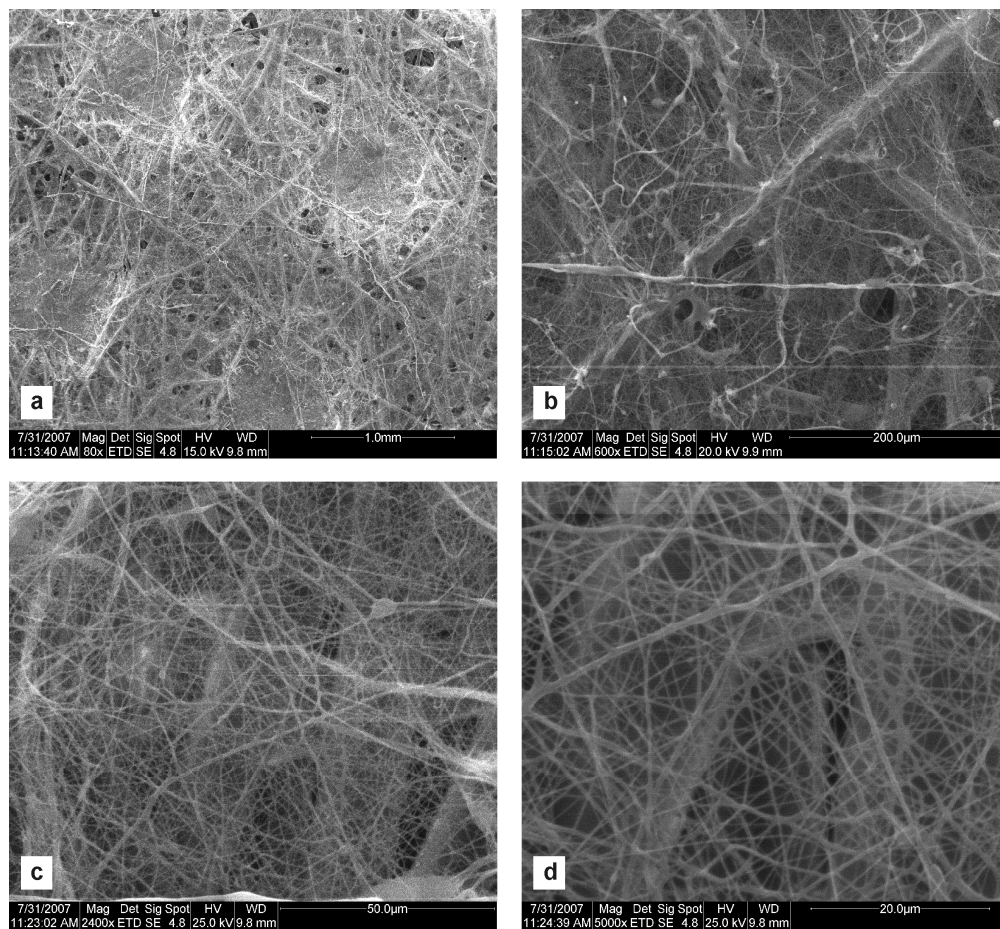
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Figure 7.- SEM microphotographs of a PVA nanofiber web deposited onto a polypropylene nonwoven substrate collector modified with an antistatic surface finishing, at different magnifications, a) 80x, b) 600x, c) 2400x y d) 5000x.
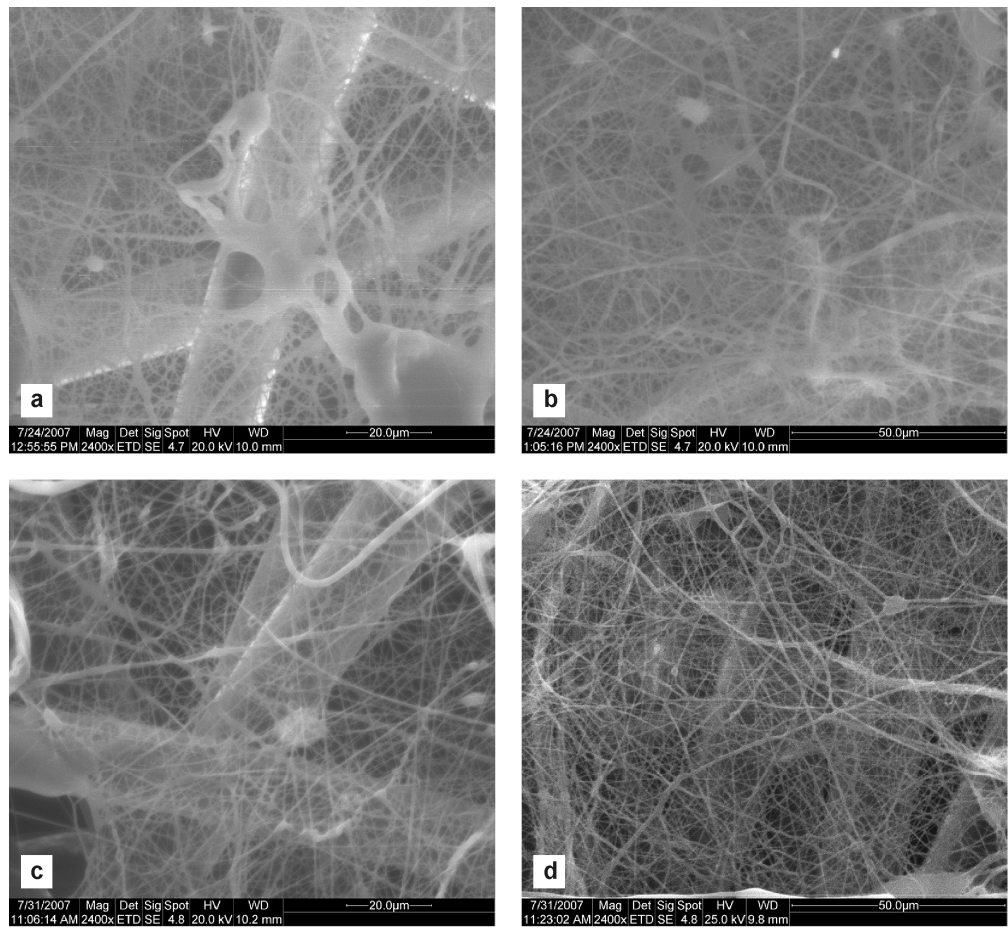
Figure 8.- SEM microphotographs of a PVA nanofiber web deposited onto a polypropylene nonwoven substrate collector chemically modified by padding with different anionic antistatic concentrations, a) 15.0 g L-1, b) 17.5 g L-1, c) 20.0 g L-1y d) 22.5 g L-1.