

ELECTROSPUN NANOFIBERS PREPARED BY TWO METHODS: *IN SITU* EMULSION POLYMERIZED PVA/NANOTIO₂ AND MIXING OF FUNCTIONAL-PVA WITH NANOTIO₂

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Abstract:

Poly(vinyl alcohol)/nano-sized titanium dioxide (PVA/nanoTiO₂) water dispersions were electrospun in order to prepare networks of polymer composite nanofiber for coating applications. In particular, the effect of the functionalization of the polymer matrix, coating of the filler particles, and the preparation method of the polymer dispersions on the nanoparticle distribution along the resulting fibers were studied. The dispersions were prepared using two different techniques: batch in situ emulsion polymerization and mixing methods. Differently coated hydrophilic nanoTiO₂ particles were used on one hand, and on the other, pure PVA and carboxyl- and silanol-functionalized PVAs were used. Dispersion properties were assessed by measuring viscosity and estimating the degree of homogeneity before electrospinning. The structure of the electrospun fibers was studied using scanning electron microscopy and elemental analysis. It was observed that the dispersion properties differed substantially depending on the types of polymer and filler particles used. Electrospinning succeeded in forming continuous fibers instead of separate droplets with all except one type of PVA/nanoTiO₂ dispersions. It was confirmed that the resulting fibers and droplets contained nanoTiO₂ particles. For the in situ polymerized dispersions the filler distribution in the resulting fibers was strongly influenced by the nanoparticle coating. In the mixing method, the resulting nanoparticle distribution was affected primarily by the polymer type used, and the role of the nanoparticle coating was not important.

Keywords:

Electrospinning, nanocomposites, PVA, nanoTiO₂, fiber morphology

Introduction

Nanofillers offer possibilities to improve the physical properties of polymers such as optical, thermal, and barrier properties with low loadings while maintaining the processability of the polymer matrix essentially intact. [1,2,3] Moreover, nanoparticles provide a way to transfer their functional properties to polymer composites.

Extremely light polymer based coatings can be produced using electrostatic coating methods and techniques that exploit the polarization force to produce nanoscale polymer fiber (electrospinning) or droplet (electrospraying) coatings from polymer solutions or melts. Nowadays, the fiber morphology resulting from electrospinning of main polymer solutions such as poly(vinyl alcohol) (PVA) and polyamide (PA) can be controlled by viscosity and electric field. [4,5] The diameter of polymer fibers generated in electrospinning is typically in the nanometer range and the resulting coating network has a large specific area. Electrospun fibers with fillers can be applied in a wide variety of applications, such as in catalysts, biosensors, and semiconductors. [6,7,8] Electrospinning of a few traditional fillers with polymers has already been demonstrated. In addition, nanoscale fillers such as carbon nanotubes have been electrospun with polymer. These studies have concentrated mostly on the effect of the concentration of the filler [4,9,10,11,12,]. The effect of the compatibility of the polymer and the filler has been less studied.

Poly(vinyl alcohol) (PVA) is widely used as a paper coating material because of its good chemical resistance, film forming ability, and, above all, water solubility. [13, 14] In addition, TiO₂ is used on paper because of its ability to enhance the whiteness of the paper substrate without affecting the adherence between the PVA layer and the paper surface [15]. Also, its anti-bacterial nature by UV activated photo catalysis [16] can be utilized in disposable sheets and wipes. An intriguing alternative to traditional bulk coating would be nanofiber coating with PVA fibers containing well-dispersed TiO₂ nanoparticles. Especially in electrospinning, PVA/nanoTiO₂ fibers could make very lightweight coatings, and because the solvent evaporates during the spinning process, with proper process parameters a dry, thin mat can be deposited on a substrate.

In order to obtain fiber containing well-dispersed nanoparticles by electrospinning, the original dispersion must be homogeneous in the nanoscale. In addition, it is to be expected that the enhanced compatibility in the dispersion would result in more even filler particle distribution along the fiber. Typically, compatibility is pursued either by using coated filler particles, [20] or by using an additional compatibilizer component. [17] However, adequate coating agents and compatibilizers are frequently not easily available. Chemical modification of the polymer matrix itself offers an interesting additional method of improving compatibility. PVA is available with different degrees of hydrolysis, and its functionality can be modified by copolymerization. These

methods have been utilized to control solubility and adhesion properties, but only in a few recent studies have they been used to improve compatibility in dispersions. [21,22] Inasmuch as the compatibility in the dispersion can be expected to influence the resulting fiber morphology in electrospinning, these methods could be used to tailor the fiber properties. However, the tailoring of interfacial adhesion in the dispersion, thus influencing the fiber morphology and distribution of the filler particles within the electrospun fibers, has not been very much reported on.

It should be noted that electrospinning is sensitive to, among other things, the viscosity of the dispersion, which can change due to the chemical modification of its components. The adding of filler particles to the polymer solution is referred to in this paper as the mixing method, and, alternatively, when they are already added during the polymerization, this is referred to as *in situ* polymerization. The *in situ* polymerization has been reported to lead to a polymer nanohybrid with a finely-dispersed nanofiller [18,19], because the filler particles are encapsulated evenly in the polymer matrix, if the filler is compatible in the monomer-solution. Thus *in situ* polymerization in the presence of the filler could be used to obtain nanoscale homogeneity without chemical modification of the polymer.

In this work, both *in situ* polymerization and mixing methods were used to prepare PVA/nanoTiO₂ dispersions, which were then electrospun on a nonwoven substrate. The aim was to obtain an even nanoTiO₂ distribution on the PVA surface. Three differently (polyalcohol, glycerol, and alumina) coated nanoTiO₂ particles were used in both methods in order to affect the fiber formation and filler distribution along the fibers. In the mixing method, in addition to the functionality of the filler coating, the effect of different functionalities of the matrix polymer was studied. Neat PVA and carboxyl- and silanol-functionalized PVAs were used, owing to their potential use in paper making.

Experimental Data

Materials

In situ polymerized PVA in this study is abbreviated as s-PVA. The vinyl acetate monomer for poly(vinyl acetate) (PVAc) synthesis was from Aldrich, the K₂S₂O₈ initiator was from Merck, and the sodium dodecyl sulfate emulsifier was from Fluka. The terminators of the PVAc polymerization were hydroquinone from Fluka and NaCl from Aldrich. The methanol used in the synthesis of PVA was from Merck.

Three commercial PVAs were obtained from Kuraray Specialities Europe: neat PVA, Mowiol 28-99, a fully hydrolyzed polymer (99.4 mol-%) with viscosity 28 ± 2 cP (20 °C and 4 wt% solution), M_w H¹²⁵ 000g/mol, abbreviated as n-PVA; anionic charged PVA, KL-318 PVA modified with carboxylic groups, degree of hydrolysis 85-90, DP 1750, viscosity 20-30 cP (20°C and 4 wt% solution), abbreviated as a-PVA; and

functionalized non-charged PVA, R1130 with silanol groups, DH 98-9, viscosity 20-30 cP (20 °C and 4 wt% solution), abbreviated as f-PVA. The carboxyl- and silanol-functionalized PVAs are copolymers. The n-PVA and f-PVA had the same molecular weight and degree of hydrolysis. [20]

Three nanoTiO₂ (rutile) grades were obtained from Kemira Pigments: M212®, coated with trimethylolpropane, abbreviated as nanoTiO₂ (oh) (crystal size ca. 20 nm, specific surface area 60 g/m²); L181®, coated with glycerol, abbreviated as nanoTiO₂ (gl) (crystal size ca. 17 nm, specific surface area 70 g/m²); and M111®, coated with alumina, abbreviated as nanoTiO₂ (al) (crystal size ca. 14 nm, specific surface area 100 g/m²). The particles are summarized in Table 1.

Black nonwoven fabric composed of cellulose based fiber and polymeric binders with grammage of 50 g/m² was used as substrate.

Table 1. Characterization of the nanoTiO₂ pigments used in this study.

Grade	Abbreviation	Main functionality of Coating	Crystal size, nm	Specific surface area, m ² /g	Bulk density, g/cm ³
M212	nanoTiO ₂ (oh)	alcohol	20	60	150
L181	nanoTiO ₂ (gl)	glycerol	17	70	150
M111	nanoTiO ₂ (al)	alumina	14	100	680

Preparation of PVA/nanoTiO₂ dispersions

PVA/nanoTiO₂ dispersions for electrospinning were prepared in two different ways: by a batch *in situ* emulsion polymerization, which is described first; and by preparing water-based dispersions of PVA or functional PVA with nanoTiO₂ by mixing, which is described thereafter.

The *in situ* polymerized poly(vinyl alcohol)/nanoTiO₂ (s-PVA/nanoTiO₂) was prepared in two steps: first the vinyl acetate monomer was *in situ* emulsion polymerized in the presence of nanoTiO₂ particles, resulting in PVAc/nanoTiO₂ water-based dispersions. The second step was alcoholysis. The emulsion polymerization was carried out in a batch reactor (1 dm³). The nanoTiO₂ (10 g) was dispersed in water in the reactor, and distilled vinyl acetate monomer (101 g) was added to the reactor under argon atmosphere. The emulsifier, sodium dodecyl sulfate, of 1 wt% and the initiator, K₂S₂O₈, 0.15 wt% was added to the dispersion. The rotation speed of the mixer was constant and the same for all the samples- the influence of various mixing speeds was not studied. The batch reactor was immersed in a water bath which had a constant water flow exchange, with incoming water temperature of 50°C. The reaction time of the polymerization and the maximum temperature attained by the outflowing water were both recorded. The maximum polymerization temperatures were kept below the boiling point of the vinyl acetate monomer (72.7°C). The synthesis was terminated with an aqueous solution of hydroquinone and a solution of supersaturated NaCl. Subsequently the sample was washed with warm water and, after drying, was added to methanol with continuous stirring. Soxhlet extraction with methanol was carried out to remove monomer residues from the s-PVA/nanoTiO₂. In the second method, neat PVA (n-PVA), carboxyl-functional (a-PVA) or silanol-functional PVA (f-PVA) was dissolved in water

at ca. 80 °C in a beaker while stirring with a magnetic bar, and nanoTiO₂ particles were added. The degree of homogeneity was visually observed. The dispersions contained water/polymer/nanofiller in the ratio of 45/4.5/1. The concentrations of the PVA and nanoTiO₂ were set to a level that enabled us to investigate the effect of the interaction between the components on the structure and properties of the electrospun fibers.

Characterization and electrospinning

Molecular weight distributions of s-PVA/nanoTiO₂ samples were characterized from the pre-stage, poly(vinyl acetate)/nanoTiO₂ dispersions, because PVAc/nanoTiO₂ dissolves tetrahydrofuran, while poly(vinyl alcohol) does not. The alcoholysis of poly(vinyl acetate) is a reaction of the functional groups and thus does not cause a chain scission which could affect the molecular weight of the s-PVA/nanoTiO₂. The weight average (M_w), number average molecular weight (M_n), and molecular weight distribution (MWD) were determined using a Waters 717 plus autosampler gel permeation chromatograph, operating at room temperature.

Viscosities of all dispersions were measured before electrospinning using a Brookfield DV-II+ viscometer, at room temperature. A low mesh wire-net was used to filtrate big polymer agglomerates before dispersion viscosity measurements.

The apparatus used in the electrospinning experiments consisted of a glass solution chamber with a nozzle and a metal needle, a copper collector plate, and a voltage source Simco Chargemaster BP 50. The apparatus was placed in a fume chamber. The copper plate and the nozzle were attached to separate stands so that the working distance (distance between the tip of the needle and the collector plate) could be altered. The voltage source was attached to the nozzle and the collector, with the nozzle charged positively and the collector plate negatively. The shape and strength of the generated horizontal electrostatic field could be modified by altering the voltage and the working distance. Needles of different diameters and lengths were used in the nozzle. The feeding rate of the dispersion was determined by pressure due to gravity and the properties of the needle.

The voltage and the distance were adjusted for each sample separately in order to produce a visible layer on the substrate. On the other hand, the voltage used was minimized. The n-PVA/nanoTiO₂ were spun with voltage of 40 kV (nozzle +20 kV, collector -20 kV) and a distance of 270 mm, a-PVA/nanoTiO₂ with voltage of 90 kV and distance of 250 mm, and f-PVA/nanoTiO₂ with voltage of 70 kV and a distance of 240 mm. s-PVA/nanoTiO₂ were spun with a voltage of 40 kV and a distance of 185 mm with nanoTiO₂ (gl, al) and 150 mm with nanoTiO₂ (oh).

The morphologies of the fiber networks resulting from electrospinning were characterized using a JEOL JSM-T100 scanning electron microscope (SEM), and the fiber diameter (excluding beads along the fibers) was measured from SEM images using ImageTool 3.0 with at least 100 measurements

per sample. Dispersion of the nanofiller within the nanofiber was characterized by elemental analysis using a JEOL JSM-6335F field emission scanning electron microscope (FESEM).

Results and Discussion

PVA/nanoTiO₂ dispersions

The in situ polymerizations were initiated by mixing the monomer, surfactant, initiator, and nanoTiO₂ particles. The nanoTiO₂ (al) dispersed well during polymerization and no agglomerates that could be visually observed were formed. On the other hand, the nanoTiO₂ (gl) dispersed poorly and some visible agglomerates formed, and the nanoTiO₂ (oh) phase separated during polymerization. This was unexpected because all the components were hydrophilic and thus it was assumed they were compatible with each other in water. The different behavior of the three filler types can be explained by the filler particle size, relative surface area, and bulk density, not only the coating type. The nanoTiO₂ (al), which dispersed well, has the finest particle size, largest relative surface area, and the highest bulk density and, on the contrary, the nanoTiO₂ (oh), which phase separated, had the largest particle size, the smallest relative surface area and low bulk density. The nanoTiO₂ (gl) falls in between. The mixing speed was kept constant during polymerization. Possibly a more homogeneous dispersion of nanoTiO₂ (oh) and nanoTiO₂ (gl) could have been achieved with higher mixing speeds.

Figure 1 and Table 2 present the measured properties of the polymers prepared by the *in situ* polymerization method. Regardless of the type of nanoTiO₂ particles used, the polydispersities obtained were relatively narrow and the molecular weight averages similar to polymerizations without filler particles. The higher polydispersity value for the hydroxyl-coated filler could be related to the phase separation of the

Table 2. Molecular weights (M_w and M_n), molecular weight distributions (M_w/M_n), maximum temperature reached during polymerization (T_{max}), and polymerization time of the poly(vinyl acetate)/nanoTiO₂ samples.

s-PVAc +	M _w [g/mol]	M _n [g/mol]	Polydispersity (M _w /M _n)	T _{max} [°C]	Time [min]
nanoTiO ₂ (oh)	962,000	210,000	4.6	56.5	32
nanoTiO ₂ (gl)	1,145,000	321,000	3.6	60.1	15
nanoTiO ₂ (al)	846,000	230,000	3.7	55.7	26

filler particles and the emulsion, and thus the smaller amount of nucleation micelles during the polymerization process. The highest molecular weight average was obtained with the sample that had the highest maximum temperature during polymerization, and vice versa, as was expected.

In the dispersions prepared by the mixing method, the different types of nanoTiO₂ particles dispersed more homogeneously than in the dispersions prepared using in situ polymerization. However, f-PVA formed gel colloids regardless of which coating of nanoTiO₂ was used, and the degree of dispersion was harder to observe. In any case, phase separation did not take place. The gel formation was probably due to a non-optimal pH value for dissolution of f-PVA. The even dispersal

of the filler particles is presumably due to good compatibility, which is related to the high degree of hydrolysis of the n-PVA and f-PVA. Carboxyl modification increases the number of hydroxyl groups along the a-PVA, which, in turn could compensate for the lower degree of hydrolysis in this case.

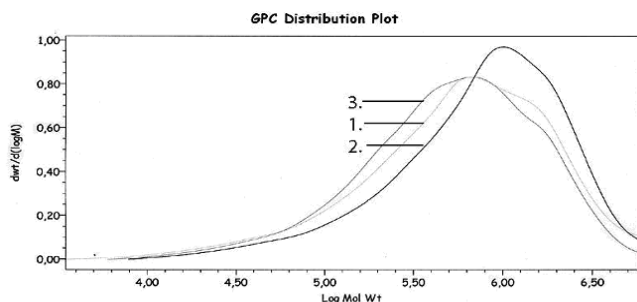


Figure 1. Chromatograms of PVAc/nanoTiO₂: 1) PVAc/nanoTiO₂ (oh), 2) PVAc/nanoTiO₂ (gl), and 3) PVAc/nanoTiO₂ (al), which are pre-stages for PVA/nanoTiO₂ dispersions.

Table 3 presents the measured viscosities of the prepared dispersions. It can be observed that the viscosities of the dispersions containing nanoTiO₂ (al) were the lowest for all polymer types. This could be explained by the better dispersal of nanoTiO₂ (al) in water solutions. It can also be observed that the viscosities of s-PVA/nanoTiO₂ dispersions with different fillers varied the most from each other: the viscosity of s-PVA/nanoTiO₂ (gl) (760 cP) is noticeably higher than that of s-PVA/nanoTiO₂ (oh) (260 cP) and s-PVA/nanoTiO₂ (al) (90 cP). The molecular weight and molecular weight distribution of the s-PVAs (Table 2) could partly explain this variance in the viscosities, but the differences were larger than could be expected on this basis. However, the filtration of the dispersions before electrospinning probably influenced the dispersion properties by removing large polymer agglomerates, which in turn results in a decrease of the polymer concentration in the dispersion, and thus its viscosity. The dispersion viscosities of the n-PVA/nanoTiO₂ and the a-PVA/nanoTiO₂ were all in the same range, varying from 370

Table 3. Dispersion viscosities of in situ synthesized PVA (s-PVA), PVA (n-PVA), carboxyl-functional PVA (a-PVA), and silanol-functional PVA (f-PVA) in the presence of trimethylolpropane (oh), glycerol (gl), and alumina (al) coated nanoTiO₂.

Polymer	Viscosity [cP]		
	nanoTiO ₂ (oh)	nanoTiO ₂ (gl)	nanoTiO ₂ (al)
s-PVA ^a	260	760	90
n-PVA ^b	470	590	370
a-PVA ^b	550	490	470
f-PVA ^b	gel	gel	gel

cP to 590 cP. The viscosity measurement of f-PVA/nanoTiO₂ dispersions failed due to the gel formation.

^a Mass ratio between vinyl acetate monomer and nanoTiO₂ was 10:1.

^b Mass ratio between PVA and nanoTiO₂ was 4.5:1.

Fiber morphology

The central aim of this research was to study the filler carrying ability of the differently prepared dispersions. Specifically, the

structures of the electrospun networks and the nanoTiO₂ distribution along the fibers (/drops) were investigated. As described above, the preparation methods of the various *in situ* polymerized mixtures and, respectively, the dispersions prepared by the mixing method, were identical. The dispersions were filtrated before electrospinning. The electrospinning parameters were adjusted for each dispersion in such a way that a visible smooth coating layer would be deposited on the non-woven substrate. The resulting fiber network was studied by SEM and the filler particle dispersion along the fibers by SEM and elemental analysis. The s-PVA, n-PVA and a-PVA with nanoTiO₂ formed fiber networks. In the case of f-PVA/nanoTiO₂, the gelled dispersions were filtered, and the dilute residues with unknown polymer/nanoTiO₂ concentration were electrospun. The resulting droplets indicate that the polymer concentration was too low and a continuous jet was not formed in the electrospinning process. When a polymer solution jet gets broken, fiber formation fails and the solution is deposited onto the substrate as droplets (spray). [21,22]

The diameters of the electrospun fibers (excluding beads along the fibers) were measured from SEM images with more than 100 measurements per sample. The mean fiber diameters and their standard deviations are shown in Table 4. The mean fiber diameters and their deviations for the three types of polymers used were similar for all the different filler coatings except for the s-PVA/nanoTiO₂ (oh) combination, which resulted in substantially thicker and more uneven fibers. On the other hand, the diameters of n-PVA/nanoTiO₂ fibers were nearly twice those of a-PVA/nanoTiO₂ fibers, with the s-PVA/nanoTiO₂ lying in between those values except for the anomalous case of hydroxyl-coated filler particles.

The fiber diameter is generally strongly affected by the dispersion viscosity and the electrospinning parameters. Higher viscosity and lower electrospinning field strength typically result in larger fiber diameter [4]. The viscosities of the n- and a-PVA/nanoTiO₂ dispersions were in the same range, and thus it seems that the observed difference in fiber diameters between these series is due to the twofold difference in spinning field strength. This is also supported by the fact that the field strength used and the resulting fiber diameters for s-PVA/nanoTiO₂ were in between those for n-PVA and a-PVA (except for the hydroxyl-coated filler). It also seems natural to assume that the anomalously thick and uneven fibers obtained for the s-PVA dispersion containing the hydroxyl-coated filler are related to the phase separation of the filler particles and the emulsion in the polymerization process and the larger value of polydispersity in this case. The distribution of the filler particles in the electrospun fibers/drops was studied by SEM, and the observations were confirmed using elemental analysis. The SEM images of fiber networks of s-PVA/nanoTiO₂ for the three types of filler particle coatings are shown in Figure 2, and Figure 3 presents images of the fiber/droplet structures which resulted from electrospinning of the a-PVA, n-PVA and f-PVA dispersions containing nanoTiO₂ (gl) fillers – the other two filler types resulted in similar structures for these polymer types.

In the s-PVA series (Figure 2) the visually observed dispersal of the nanoTiO₂ particles during the *in situ* polymerization was found to correlate with their distribution along the electrospun

fibers. The nanoTiO₂ (oh), the phase of which separated during the polymerization, was found to be widely scattered along the electrospun fibers, whereas the poorly dispersible nanoTiO₂ (gl), and well-dispersed nanoTiO₂ (al) were distributed more densely along the resulting fibers. For the nanoTiO₂ (al) filler type, some very large filler agglomerates were found as well, despite their having the best visual dispersal during polymerization. This is probably due to the too-high concentration of the filler in the corresponding dispersion. Even though the nanoTiO₂ particles were coated in order to prevent their mutual interaction and in order to enhance the interaction between the filler particles and the polymer, agglomerate formation cannot be prevented for high filler concentrations, especially during electrospinning, during which the concentration is increased.

When the polymer matrix was n-PVA or a-PVA (Subfigures 3a and 3b, correspondingly), the nanoparticles were evenly distributed and embedded in the polymer matrix, but smooth looking

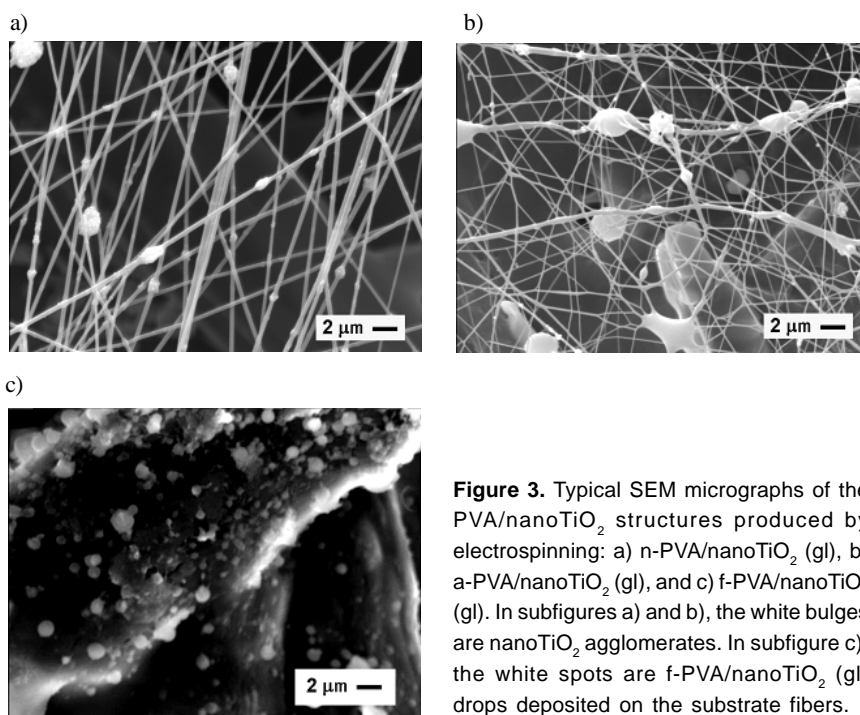


Figure 3. Typical SEM micrographs of the PVA/nanoTiO₂ structures produced by electrospinning: a) n-PVA/nanoTiO₂ (gl), b) a-PVA/nanoTiO₂ (gl), and c) f-PVA/nanoTiO₂ (gl). In subfigures a) and b), the white bulges are nanoTiO₂ agglomerates. In subfigure c), the white spots are f-PVA/nanoTiO₂ (gl) drops deposited on the substrate fibers.

beads were detected in the a-PVA fibers and rough surface bulges in both the a-PVA and n-PVA fibers. Elemental analysis

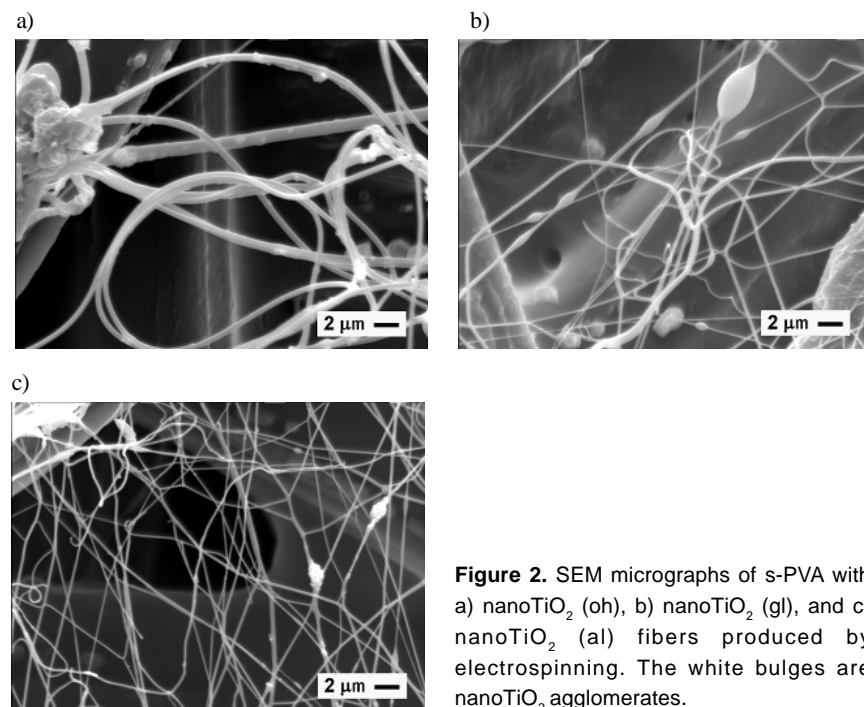


Figure 2. SEM micrographs of s-PVA with a) nanoTiO₂ (oh), b) nanoTiO₂ (gl), and c) nanoTiO₂ (al) fibers produced by electrospinning. The white bulges are nanoTiO₂ agglomerates.

confirmed that the smooth beads consisted of the polymer, and the rough bulges were found to be filler agglomerates. The n-PVA fibers contained substantially more filler agglomerates than the a-PVA fibers. Subfigure 3c presents the drops deposited on the substrate fibers which resulted from the electrospinning (spraying) of the f-PVA/nanoTiO₂ (gl) dispersion. The resulting drops of both the f-PVA/nanoTiO₂ (oh) and (gl) appeared smooth. Elemental analysis confirmed that nanoTiO₂ was present in the drops.

Based on the smooth surface structure of the drops, it can be presumed that the nanoTiO₂ particles are evenly distributed within the drops, not as agglomerates.

Conclusions

The challenge of polymer nanocomposites has been to produce well-dispersed structures in nanoscale. In this study, we prepared polymeric nanocomposite fibers using electrospinning PVA/nanoTiO₂ dispersions. Two different approaches were used: *in situ* polymerization in the presence of nanoTiO₂ and mixing pure PVA or carboxyl- or silanol-functionalized PVAs with nanoTiO₂s. Hydroxyl-, alumina- and glyceryl-coated nanoTiO₂ fillers were used for each polymer type. The aim was to study the nanofiller-carrying ability of the dispersions and distribution of the nanoTiO₂ particles along the PVA fibers which resulted from their electrospinning, not *in situ* polymerization kinetics, optimization of polymerization

Table 4. Diameters (mean and standard deviation) of fibers (and droplets) of the electrospun (/sprayed) PVA/nanoTiO₂ samples.

Polymer	nanoTiO ₂ (oh)		nanoTiO ₂ (gl)		nanoTiO ₂ (al)	
	Diameter, nm		Diameter, nm		Diameter, nm	
	Mean	Std. Dev	Mean	Std. Dev	Mean	Std. Dev
s-PVA	600	500	230	110	200	70
n-PVA	310	90	320	90	260	120
a-PVA	150	50	150	80	180	80
f-PVA (droplets)	550	320	800	320	-	-

conditions, or optimization of the process parameters. The preparation conditions of the dispersions in the two methods were kept constant. Due to variation in the properties of the prepared dispersions for different polymer types, the electrospinning parameters were separately adjusted for each dispersion in order to produce a visible layer on the substrate. All but the silanol-functionalized PVA/nanoTiO₂ dispersions yielded continuous fibers in electrospinning. The resulting fiber diameters varied for the various polymer types, which is probably related to the different electric field strengths used for them in electrospinning. For each polymer type, the filler coatings used were found to have a minor effect on the fiber diameter. The *in situ* polymerized PVA/hydroxyl-coated nanoTiO₂ combination was an exception: it resulted in substantially thicker and more uneven fibers than those for the other two nanofiller coating types. This anomaly was probably related to the phase separation of this filler particle type during the polymerization. The silanol-functionalized PVA/nanoTiO₂ dispersions formed gels. Two of them resulted in drops instead of fibers, and one of them could not be electrospun at all.

For the *in situ* polymerized PVAs the visually observed compatibilities of the nanoTiO₂ particles during the polymerizations were found to correlate to their distribution along the electrospun fibers: the alumina-coated filler resulted in the most homogeneous dispersion and most dense filler distribution along the fibers, while hydroxyl-coated particles phase separated from the dispersion and were scarcely scattered in the fibers. The density of the filler particles in the fibers might have been improved with a more vigorous mixing during polymerization.

All the filler particle types resulted in homogeneous dispersions with the carboxyl- and silanol-functionalized PVAs and pure PVA, and dense filler distribution in the resulting fibers/drops. In addition to filler particles embedded in the polymer fibers, the pure PVA and carboxyl-functionalized PVA fibers also contained large filler agglomerates. However, carboxyl functionalization substantially reduced the size and density of the filler agglomerates, as compared to pure PVA. The filler distribution in the fibers was even for all polymer dispersions, in the sense that, excluding the polymer beads, no sections void of filler particles were found.

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