

MECHANICAL PROPERTIES OF PVA NANOFIBER TEXTILES WITH INCORPORATED NANODIAMONDS, COPPER AND SILVER IONS

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ABSTRACT. The unique properties of nanotextiles based on poly(vinyl-alcohol) (PVA) manufactured using the electrospinning method have been known and exploited for many years. Recently, the enrichment of nanofiber textiles with nanoparticles, such as ions or nanodiamond particles (NDP), has become a popular way to modify the textile mechanical, chemical and physical properties of the textile. The aim of our study is to investigate the macromechanical properties of PVA nanotextiles enriched with NDP, silver (Ag) and copper (Cu) ions. Nanofiber textiles of various surface weights were prepared from a 16% PVA solution, while glyoxal and phosphoric acid were used as cross-linking agents. The copper and silver ions were diluted in an aqueous solution and NDP were dispersed into the fibers by ultrasound homogenization. All but one of the sets of samples were exposed to a temperature of 140 °C for 10 minutes. The samples without thermal stabilization exhibited significantly lower elastic stiffness and tensile strength. Moreover, the results of tensile testing indicate that the addition of dispersed nanoparticles has a minor effect on the mechanical properties of the textiles and contributes rather to their reinforcement. However, the lack of thermal stabilization results in a poor interconnection of individual nanofiber layers, and the non-stabilized textiles exhibit lower elastic stiffness and reduced tensile strength.

KEYWORDS: PVA nanofiber textiles; nanodiamonds; ions; mechanical properties; tensile strength.

1. INTRODUCTION

The production of submicrometer fibers using the electrospinning principle is nowadays widely known in two forms – the needle method and the needleless method. The needle method exploits high voltage to create an electrically charged stream of polymer solution or alloy coming out of the needle. While the compound is squirting due to the voltage between the two electrodes, it loses its redundant water. Therefore, when the fiber lands on a supporting material, it consists of the polymer only.

NanospiderTM is a modified electrospinning method allowing the production of extremely thin nanotextiles made from a liquid polymer using needleless technology. In particular, a revolving cylinder electrode is partially submerged in a liquid polymer and the solution is attracted to the counter-electrode with an opposite polarization. The deposited fibers are arranged randomly on its surface and form a non-woven nanofiber textile. The diameter of these fibers is usually in the range between 50 and 300 nm, depending on the polymer that is used [1, 2].

Nanofibers may exhibit various properties, and they

can therefore be used in numerous applications. Their properties can be substantially changed by incorporating nanoparticles into their structure [3]. This is based on a similar principle as for example steel fiber reinforcement of concrete which is nowadays quite widely used [4]. The present study is focused on the influence of dispersed NDP, silver and copper ions on the mechanical properties of nanotextiles based on an aqueous PVA solution. There are numerous ways to incorporate these particles into the polymer for electrospinning, e.g., separation, extraction or catalysis [5]. For the purposes of electrospinning, PVA may be dissolved in water or in some polar dissolving agent. Our study investigates PVA nanofiber textiles based on an aqueous solution for their specific properties and with a view to low cost production. The material can be absorbed to a human tissue, so PVA-based nanomaterials seem to a perfect covering and surgical material thanks to their ability to transport antibacterial agents directly to contaminated wounds [6].

Andrady [2] presents some properties of an aqueous PVA solution having a diverse molecule weight (M_n), concluding that the PVA nanomaterial ($M_n = 115000$

Set	Incorporated particle	Concentration (%)	Electric current (mA)	Specific area density (g m^{-2})
PVA stable	—	—	0.21	3.3 ± 0.3
PVA unstable	—	—	0.21	4.3 ± 0.2
PVA NDP 0.5	NDP	0.50 %	0.13	2.4 ± 0.4
PVA NDP 1.0	NDP	1.00 %	0.13	3.2 ± 0.3
PVA Cu 0.5	Cu-ions	0.50 %	0.21	3.1 ± 0.3
PVA Cu 1.0	Cu-ions	1.00 %	0.21	3.4 ± 0.3
PVA Ag 0.5	Ag-ions	0.50 %	0.21	3.2 ± 0.5
PVA Ag 1.0	Ag-ions	1.00 %	0.21	4.2 ± 0.7

TABLE 1. Overview of the nanofiber textiles that were produced and tested.

in a 10 % aqueous solution) exhibits better mechanical endurance and water resistance after methanol treatment. Stabilization of an aqueous PVA solution is provided by cryogenic or non-cryogenic methods, both leading to a similar outcome.

The cryogenic method uses cyclic freezing, melting and maturing of the polymer, there can be numbers of cycles, durations, and ratios between periods. A study by Bercea et al. [7] explored how the concentration, M_n and the degree of hydrolysis of a PVA solution depend on the mechanical properties of the stabilized polymer. In their study they applied 200 minute cycles of freezing, melting and maturing. Huang et al. [8] used a prolonged duration of the maturing period of an aqueous PVA solution. They then incorporated nanoplates of MgAl LDH (Layered Double Hydroxides). After applying different numbers of cryogenic cycles, they measured the stiffness of the PVA with 0.5 wt% of incorporated particles. The stiffness of the PVA-LDH was increased by 25 %, 22 % and 149 %, using 7, 9 and 11 cycles, respectively. The same trend was observed in the strength measurement – there were increases of 100 %, 100 % a 300 %.

Non-cryogenic methods introduce a completely different approach to stabilizing an aqueous PVA solution, e.g., the salting-out method described in a paper by Jensen et al. [9]. The PVA solution interacts with a solution of high ionic power, where water molecules form around the ions, so that they are no longer bonded with the PVA molecules. The other non-cryogenic methods have a common step, i.e., another chemical compound that changes the mechanical properties is added to the polymer. Yao et al. [10] used methanol for PVA stabilization, and left the compound to interact for 8 hours. The hydrogen atoms bound to water molecules were replaced by hydrogen atoms in intramolecular bonds of the polymer, and the hydrophilic character of the PVA was eliminated. As a side effect, there was an increase in the crystallinity of the PVA and consequently in its elastic stiffness. In their study, Çay a Miraftab [11] used 1,2,3,4-butane tetra carboxylic acid (BTCA) to stabilize PVA. The final hydrogel was water-resistant, and, in addition, its thermal properties were improved.

A similar method is described in a paper by Franco et al. [12]. Their paper presents the stabilization of a PVA solution for electrospinning using methanol and glutaraldehyde vapor (80 °C) treatment. The PVA compound was repeatedly warmed up to 150 °C in order to evaporate the redundant glutaraldehyde. They observed an improvement in tensile and compressive strength, and increased biocompatibility compared to the original state. A similar thermal stabilization approach was also used by Tesarek et al [13].

Modification of polymers by incorporating nanoparticles has become a major focus for many research teams. In a recent study, Siegel and Kotal [14] investigated the influence of gold layers on the electrical and physical properties of polyethylene, poly-tetra-fluoroethylene and poly-ethylene-terephthalate compounds.

NDP are another very promising option used in many research fields. The stiffness, thermal conductivity and biocompatibility of NDP allow a large number of applications as particles incorporated into nanofibers to improve their mechanical and chemical properties. NDP are widely produced by the method of detonation synthesis, which is relatively cheap. However, it is necessary to ensure even distribution of NDP within the carrying material in order to attain improved properties of the entire nanocomposite. A drawback of NDP use is an increase in the weight of the nanocomposite, and it is therefore essential to add only a few units of weight percentage of NDP [15]. A study performed by Parizek et al. [16] explored the effect of poly(lactic-co-glycolic) acid (PLGA) processed by electrospinning and enriched with bioactive NDP on human-like osteoblasts. After two days, the cells formed a consistent layer, and no inflammatory activity attributed to the antibacterial effect of the nanocomposite was observed. The possibility of drug delivery using nanodiamond structures was also investigated also the study by Petrak [17], who focused on the possibility of boron doped nanodiamond films for biosensing applications.

Maitra et al. [18] studied the mechanical properties of thin PVA-NDP layers cast in Petri dishes. Each layer was 0.5 mm in thickness and the NDP diameter was about 5 nm. Transmission electron microscopy

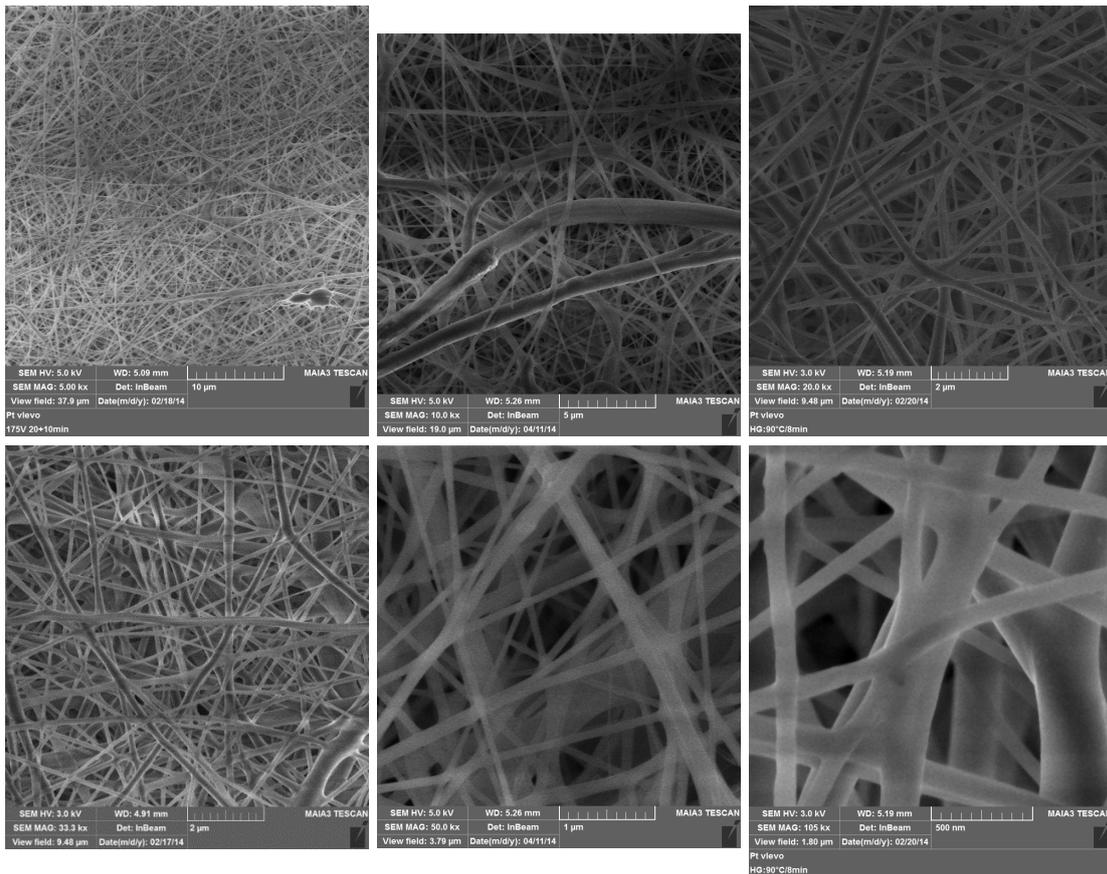


FIGURE 1. Various sets of pure stabilized PVA nanotextiles (20 k times) – top SEM images from left to right: 5 k times, 10 k times, 20 k times; bottom SEM images from left to right: 33.3 k times, 50 k times, 105 k times.

and the SAXS method demonstrated that a concentration of NDP in the range of 0–0.6 wt% provides an equal distribution of the particles in PVA. The most concentrated PVA-NDP sample showed a 34 % increase in the crystallinity, a 98 % increase in elastic stiffness and a 79 % increase in strength compared to plain PVA samples. The incorporation of a more concentrated PVA-NDP nanocomposite (2.0 wt%) was explored by Wang et al. [19]. In their study, the dispersed NDP increased the stiffness by 155 % and the tensile strength by 89 %. The authors, however, state that they observed an agglomeration of NDP due to the high concentration. The advantage of incorporating NDP compared to carbon tubes is discussed in a paper by Morimune et al. [20]. NDP (1.0 wt%) showed a more significant increase in the stiffness and thermal conductivity of the composite at lower concentration of NDP.

Ag ions are widely investigated nanoparticles for incorporation in PVA. Jin et al. [21] describes the process of incorporating silver ions obtained from silver nitrate (AgNO_3). In their approach, the compound of PVA (> 99 %, $M_n = 89000$ up to 98000) and AgNO_3 (> 99.998 %) is briefly heated up to 155 °C, and then there is an uncontrollable degradation of AgNO_3 to silver ions that are then reduced, and a large number of Ag particles are formed. This compound is processed by the electrospinning method and is spread

evenly on the supporting material.

Mahanta and Valiyaveettila [22] investigated the effect of incorporated silver ions on PVA nanofibers produced by the electrospinning method. Their PVA fibers ($M_n = 146\,000$ – $186\,000$) were 300–500 nm in diameter and the size of the silver nanoparticles was in the range of 10–20 nm. According to their findings, the incorporation of Ag into PVA increases its biocompatibility and antibacterial properties, but the Ag ions have a negative effect on PVA nanofibers. Ag ions reduce the strength of the nanofiber textile from 12.6 MPa to 7.9 MPa, the elastic stiffness from 3.02 to 1.99 MPa and the maximum elongation from 30 % to 24 %.

A study by Khanna et al. [23] focused on the preparation of Cu nanoparticles. They used a compound of hydrazine hydrate and sodium formaldehyde sulfoxylate to extract pure Cu nanoparticles 30 nm in diameter. Based on the available literature, we assume that Cu ions enrich the PVA nanotextile with antibacterial properties [24]. According to the available literature the effect of Cu ions has not yet been investigated by any author. In general, there are numerous studies dealing with the influence of nanoparticles on antibacterial properties, but no comprehensive study on their influence on macroscopic mechanical properties is available.

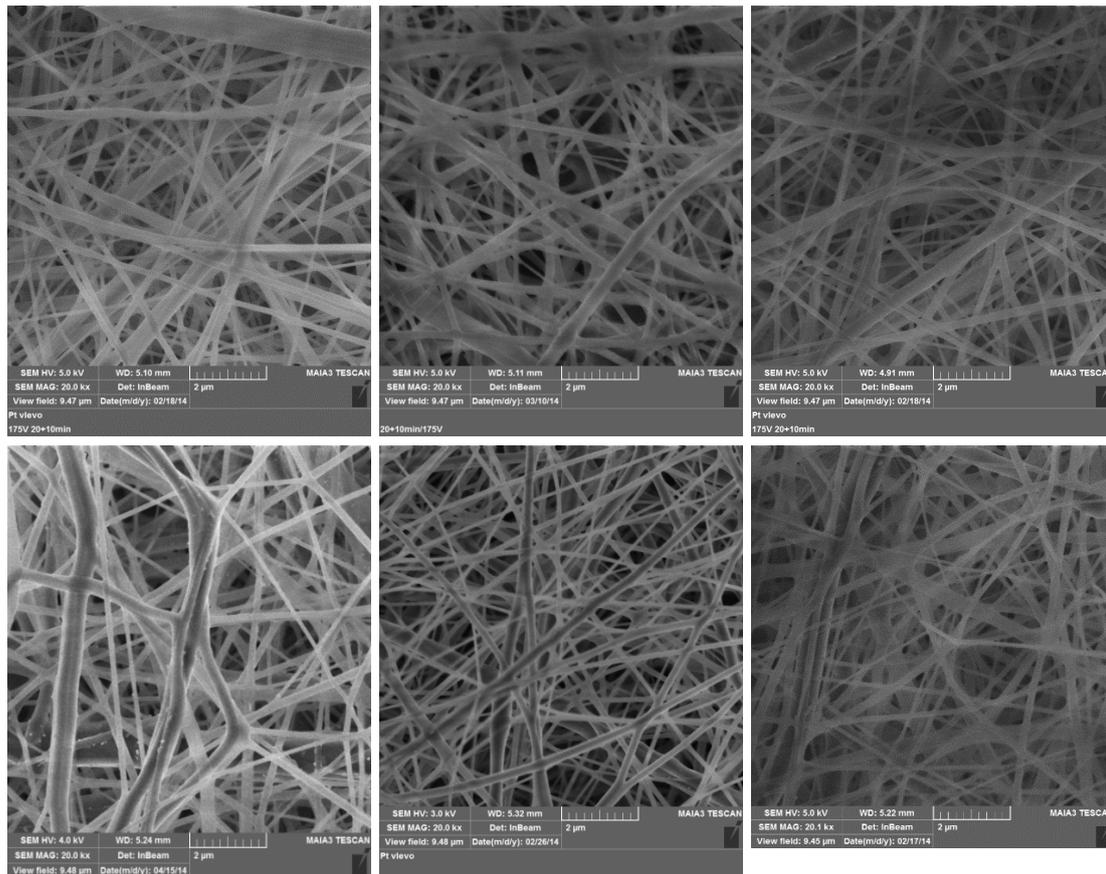


FIGURE 2. Various sets of stabilized PVA nanotextiles (20 k times) – top, SEM images, from left to right: PVA + NDP 0.5 wt% , PVA + Cu 0.5 wt%, PVA + Ag 0.5 wt%; bottom, SEM images, from left to right: PVA + NDP 1 wt%, PVA + Cu 1 wt%, PVA + Ag 1 wt%.

2. EXPERIMENTAL SAMPLES AND METHODS

The nanofibers for our study were produced for an aqueous PVA solution using the needleless electrospinning method in the laboratories of the Czech Technical University in Prague, Faculty of Civil Engineering, using the NanospiderTM NS Lab 500 S (Elmarco, Czech Republic) device. This equipment produces equally distributed nanofibers within the individual layers forming the textile. In particular, we used a cylindrical electrode (600 mm in length) rotating at a frequency of 5 Hz, positioned 140 mm from the collecting electrode. The voltage was set to 81.3 kV and the nanofiber production was carried out in laboratory conditions at a temperature of 25–28 °C and relative humidity ranging between 40–46 %. To obtain optimum properties, the spinning time for one set was 5 minutes [13].

The cylindrical electrode was half submerged into the aqueous PVA solution (16 wt%) Sloviol R (Fichema, Czech Republic). This approach was inspired by a similar study performed by the Center for Nanotechnology in Civil Engineering at CTU [25]. The polymer solution consisted of 375 g PVA Sloviol 16 %, 117 g distilled water, 4.4 g glyoxal and 3 g phosphoric acid (75 %). The last two compounds were

used as cross-linking agents, providing the appropriate consistency. During the electrospinning process, the nanofibers were deposited on a supporting polypropylene geotextile substrate with area density of 18 g m⁻² and antistatic treatment. The produced PVA fibers were stabilized by exposure to an elevated temperature of 140 °C for 10 minutes, and a reference set of the textiles was left non-stabilized. The textiles had various area densities ranging from 2 to 3 g m⁻².

The nanoparticles were incorporated into the PVA solution using two approaches. Soluble compounds of AgNO₃ and CuSO₄ · 5H₂O were dissolved in water and the ions were added to the aqueous solution of PVA, forming PVA-Cu and PVA-Ag compounds. NDP (NanoAmando, Nex Metals and Chemicals Corp, Ltd., Kyobaschi) 5 nm in diameter and were added to the PVA solution by homogenization. An overview of the produced nanofiber textiles can be found in Table 1.

The NDP of soluble compounds were added to the PVA solution in a mixer, and were homogenized for 10 minutes and placed into an ultrasound bath for 5 minutes in a closed flask. The nanoparticles were uniformly distributed all over the nanotextile. The structure of the nanofibers is documented in the SEM images introduced in Figures 1–2.

The stabilized plain nanofibers with no added nanoparticles or ions have various diameters, as

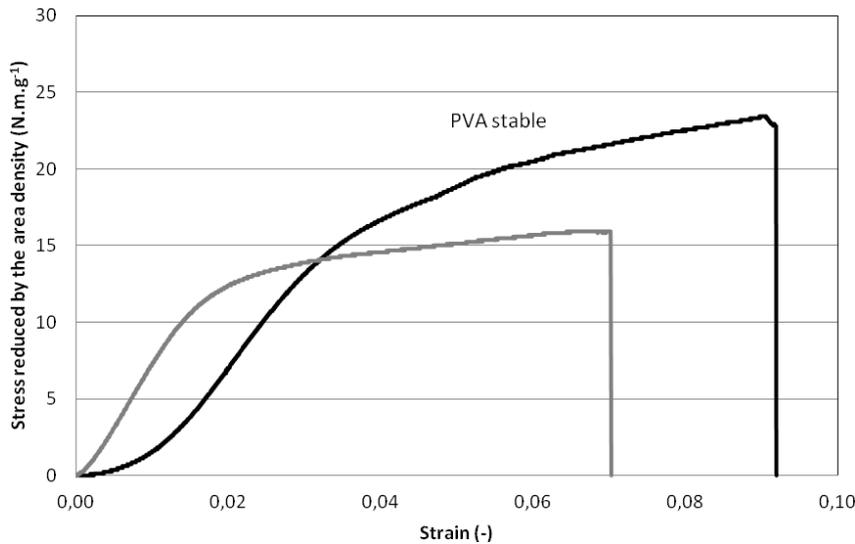


FIGURE 3. Stress-strain diagrams for stabilized and non-stabilized PVA nanofiber textiles.

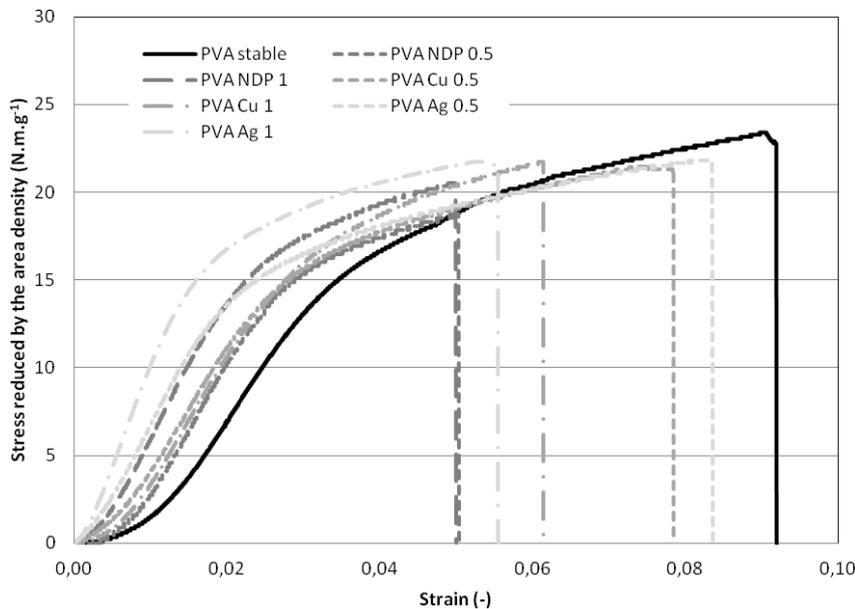


FIGURE 4. Stress-strain diagram of all of the stabilized nanotextiles.

demonstrated by the SEM images with magnification 5–105 k times (Figure 1), ranging between 100 and 400 nm. The average fiber diameter was 200 nm, which is used for PVA fibers produced using electrospinning [2]. The 5 times magnification provides evidence of the uniform distribution of individual fibers, providing a macroscopically homogeneous structure. Bonding (crosslinking) at the contact between individual fibers, as a result of thermal stabilization [10, 12, 21], is clearly visible at higher magnifications.

Representative SEM images of nanofibers with the addition of incorporated nanoparticles (NDP, Cu and Ag ions in concentrations of 0.1 and 1 wt%) are presented in Figure 2. The SEM images demonstrate that there is no significant difference between the microstructure of the plain fibers and those containing dispersed nanoparticles or ions.

Nanofiber textile specimens were produced for test-

ing in tension to investigate the influence of stabilization and nanoparticles on the strength of textiles, their ductility and elastic stiffness. For this purpose, a conventional setup for testing thin foils or metal specimens was used, utilizing a testing frame with high sensitivity, the LabTest 4.100SP1 device equipped with a load cell with a measuring range up to 50 N. The experiment was displacement controlled by a loading rate of 0.2 m/s. The testing was carried out in normal laboratory conditions (temperature 23 °C and r.h. about 40 %). 2 × 12 cm samples were cut from each textile and the ends of each specimen were reinforced by an adhesive tape to withstand attachment of the textiles into the clamps of the testing machine. The supporting geotextile was removed just before testing to avoid any damage to the specimens. In order to obtain statistically representative data, at least 6 specimens were tested for each set.

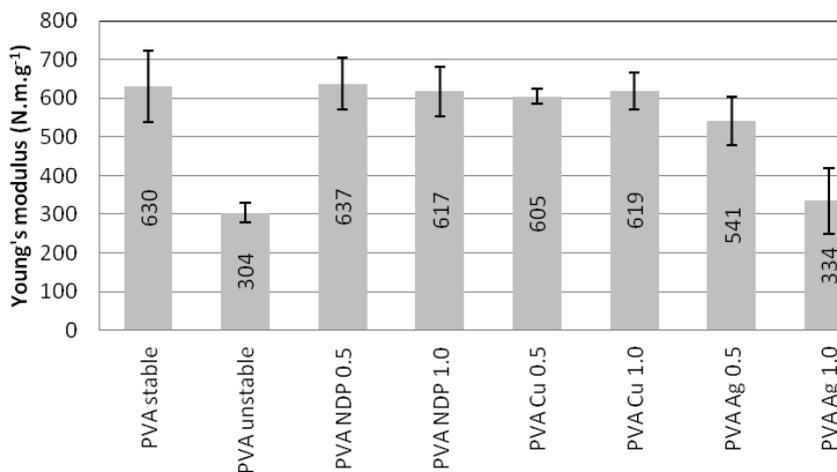


FIGURE 5. Comparison of Young's moduli for all tested textiles.

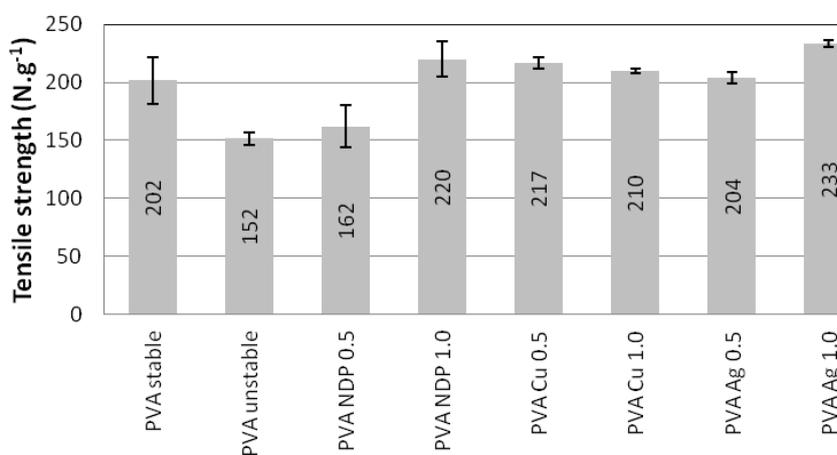


FIGURE 6. Comparison of tensile strength for all tested textiles.

3. EXPERIMENTAL RESULTS

The macroscale mechanical properties of the nanofiber textiles were investigated from two points of view. First, the effect of thermal stabilization was studied, and secondly the influence of the concentration and the type of incorporated particles was investigated [26]. Prior to tensile testing, the dimensions and the weight of each specimen were measured in order to obtain its area density. This testing process was similar to the standard testing of the steel specimens in tension, widely used, e.g., in the automotive industry [27]. However, because of the limited thickness, we introduced a physical parameter stress reduced by the area density (N m g^{-1}) in order to compare the textiles with each other and obtain a size independent measure of strength and elastic stiffness. A similar approach was used in the study by Slanec et al. [28] aimed at determining the strength parameters of thin surface coating layers.

A comparison of individual stress-strain diagrams representing stabilized and non-stabilized nanofiber textiles with no incorporated particles is presented in Figure 3. A comparison of stress-strain diagrams representing the textiles modified by incorporated particles is provided in Figure 4.

The Young's modulus value (elastic stiffness) was determined as a tangent of the linear part of the experimentally obtained stress-strain diagram, where the stress is normalized to the area weight of the tested textiles. The tensile strength was determined as the maximum stress value reached during the experiment. A comparison of the Young's moduli is provided in Figure 5, and a comparison of the tensile strength between individual sets is presented in Figure 6, including the non-stabilized set. The elongation of the textiles was determined as the ratio of the absolute maximum elongation of each sample to its original length, and the results are summarized in Figure 7.

4. DISCUSSION

The electron microscopy images indicate no major difference in the nanofiber structure of the individual sets of stabilized textiles (Figures 1–2).

The stress-strain diagrams, of the plain stabilized and non-stabilized nanofiber textiles normalized to the area density of each sample, show a significant difference in their shape and in the maximum stress that was reached (Figure 3). The instant increase in the stress of the unstabilized nanotextile suggests that the initial phase of fiber arrangement with respect

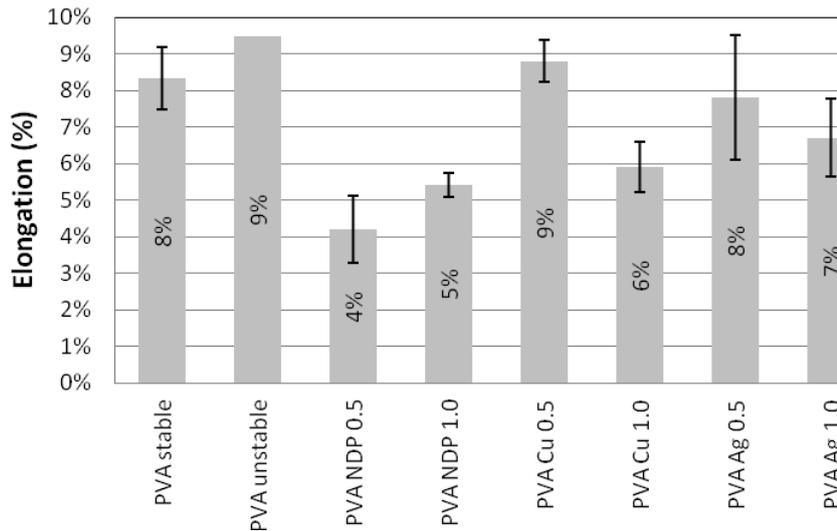


FIGURE 7. Comparison of the maximum strain (elongation) for all tested textiles.

to the direction of the tensile stresses takes place at negligible stress-levels, instantly proceeding to a linear response. It is obvious that the stabilization process changes both the chemical and the physical properties of the nanotextile. The stabilized textiles are not only interconnected within one layer but also form a compact 3D structure where the layers are connected with each other. As the stabilized textile stretches, the fibers must arrange themselves in a parallel structure with considerable resistance, leading to the linear phase at relatively high stress-levels.

On the basis of a comparison of the results of the individual modifications by means of incorporated particles it can be concluded that the mechanical properties are altered. The lowest elastic stiffness was measured on the non-stabilized PVA textiles (PVA unstable), followed by PVA Ag 1.0 where the concentration of the silver nanoparticles was equal to 1 wt%, even though these nanofiber textiles have the highest area density, up to 3 times higher than for the other sets (Table 1). This result confirms the findings presented in the study by Mahanta and Valiyaveettila [22], where the Young's modulus was also significantly lower in the PVA Ag samples than in the plain PVA textiles.

The tensile strength of the textiles with incorporated nanoparticles is in general higher than for the unmodified fibers, and is significantly higher than for the non-stabilized PVA textiles. This phenomenon may be related to the specific structure of the compound, as mentioned above. However, no elongation of the modified textiles was observed, despite the suggestions of other authors as indicated in the introductory section. According to our findings, the modified textiles exhibit reduced ductility, reflected in lower values of the elongation parameter. The difference between our results and the findings of other authors may have been caused by the nanofiber preparation procedure and also by the size of the incorporated nanoparticles.

5. CONCLUSION

This study has focused on the impact of stabilization and incorporation of dispersed nanoparticles of Ag, Cu and NDP on the mechanical properties of nanofiber textiles produced from an aqueous PVA solution. Thermal stabilization was accomplished by exposing the textiles to an elevated temperature of 140 °C for 10 minutes. NDP, Cu and Ag ions were incorporated into the solution prior to the production of the nanofibers in a concentration equal to 0.5 and 1 wt%.

The mechanical properties of the nanofiber textiles were subjected to standard tensile testing, and the results were compared with reference plain PVA samples. From the measured data, it is clear that incorporating the tested nanoparticles does not significantly affect the mechanical properties at macroscale and, if it does, it makes them superior to the plain PVA textiles, with the exception of the ductility (elongation) parameter. On the other hand, the non-stabilized PVA textiles exhibited the lowest Young's modulus values and tensile strength values.

Future research will focus on the influence of the incorporated Ag and Cu nanoparticles on the electrostatic field generated in the electrospinning process and also the impact on the production process due to increased conductivity of the solution.

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