

## The Analysis of Forming PVB-SiO<sub>2</sub> Nanocomposite Fibers by the Electrospinning Process

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The poly (vinyl butyral)-silica (PVB-SiO<sub>2</sub>) nanofibers were obtained by the electrospinning process. The experiments were carried out with PVB solution in concentration of 10 wt.% where ethanol was used as the solvent. The silica nanoparticles were added in the solution in different contents of 1, 3 and 5 wt.% SiO<sub>2</sub> and nanoparticles were modified with  $\gamma$ -aminopropyltriethoxysilane (AMEO silane). The impacts of the parameters of the electrospinning process and the silica nanoparticles on the produced PVB-SiO<sub>2</sub> nanocomposite fibers were tested. The structures of the PVB-SiO<sub>2</sub> nanocomposite fibers were investigated using optical microscopy and scanning electron microscopy (SEM). The morphology and distribution of the resulting nanofibers were analyzed using the software Image-Pro Plus.

*Key words:* nanofibers, nanocomposite fibers, nanoparticles, aminopropyltriethoxysilane (AMEO silane), PVB-SiO<sub>2</sub>, electrospinning method, experimental results.

### Introduction

ELECTROSPINNING is a unique, straightforward and versatile technology for producing polymer fibers from polymer solutions and polymer melts. The obtained fibers are with nanometre scale diameters [1].

The process of electrospinning utilizes a high voltage source to charge a polymer solution which is then accelerated towards a grounded metal collector of the opposite polarity. The fiber jet travels allowing the solvent to evaporate from it, thus leading to the deposition of solid polymer fibers on the collector. The basic electrospinning set-up consists of a syringe filled with a polymer solution, a high voltage source and a grounded conductive collector screen [2]. An electric field is initiated between the tip of the syringe and the collector and the electrostatic forces are generated. Under the influence of an electrostatic field, a pendant droplet of the polymer solution at the end of the syringe is deformed into the conical shape called Taylor cone. The charge density increases at the tip of the cone. When the electrostatic forces overcome the surface tension of the polymer solution, a jet is ejected from the tip of the syringe [3-6].

The schematic drawing of the electrospinning process is depicted in Fig.1. The electrospinning apparatus used for the experiments in this work is the Electrospinner CH-01 (Linari Engineering), located at the Faculty of Technology and Metallurgy in Belgrade (Fig.2 and 3).

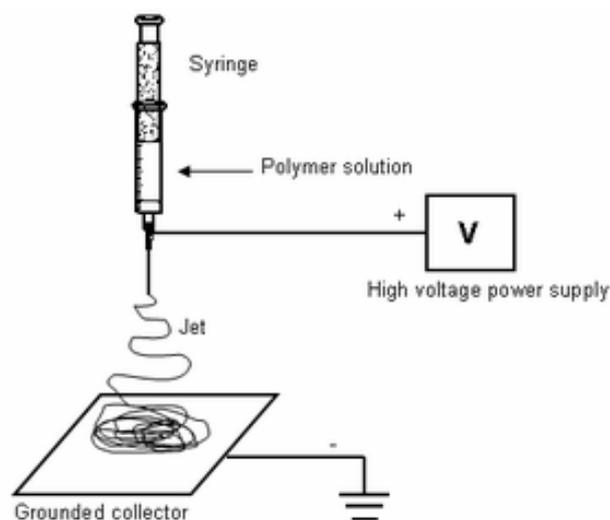


Figure 1. Basic electrospinning set-up

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**Figure 2.** The electrospinning set-up at the Faculty of Technology and Metallurgy, Belgrade



**Figure 3 -** The electrospinning apparatus at the Faculty of Technology and Metallurgy, Belgrade

### The preparation of the solutions

The PVB powder was dissolved in ethanol in the concentration of 10 wt.% and the silica nanoparticles were put into the solution in the concentration of 1, 3 and 5 wt.%. The SiO<sub>2</sub> nanoparticles were used both unmodified and modified. They were put into the PVB solution (10 wt.%) and stirred continuously for 24 hours and ultrasonically dispersed in the solution for 15 minutes additionally.

The method of modification of the silica nanoparticles with  $\gamma$ -aminopropyltriethoxysilane (AMEO silane) started with adding the silane into 95 wt. % ethanol – 5 wt. % water mixture to reach 2 wt. % final AMEO concentration. Around 10 minutes were allowed for hydrolysis and silanol formation. After the addition of the nanoparticles, the solution was homogenized with a magnetic stirrer for 30 minutes in order to break up the major agglomerates. After three hours of sonication, the particles were placed at the bottom of the beaker and the supernatant was decanted. The particles were rinsed with ethanol for three times and dried in an oven at 110°C [7].

### Electrospinning

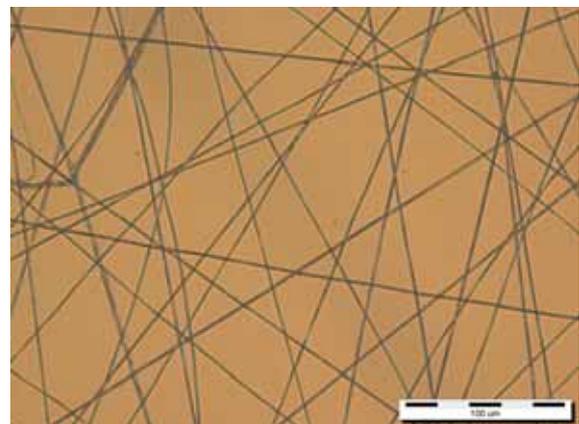
The PVB solution without silica particles as well as with them (both modified and unmodified, all with different contents) were tested changing the applied voltages and the flow rates in the electrospinning process. A set of experiments was carried out when the applied voltages were 16, 20, 24, 28 and 30 kV while the flow rate was kept constant at  $Q = 1\text{ mL/h}$ . Another experimental set was performed with the flow rates valued 0.2, 0.4, 0.6 and 0.8 mL/h while the voltage was held at  $V = 20\text{ kV}$ . During the electrospinning process, the formed nanofibers were deposited onto the flat aluminium foil which served as a collector (Fig.4). The tip-to-collector distance was  $h=10\text{ cm}$  in all cases.



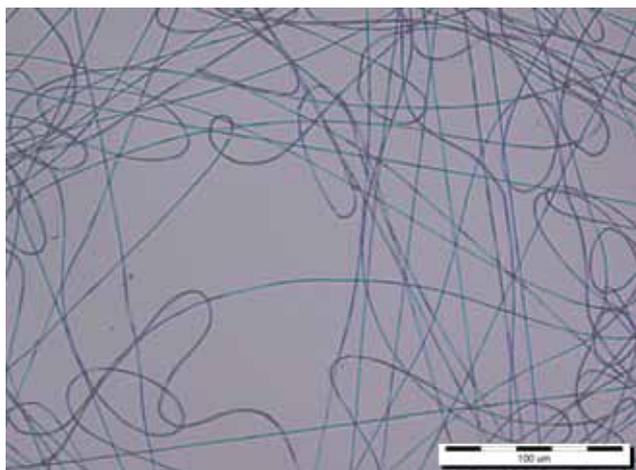
**Figure 4.** The collected nanofibers on the aluminium foils

### Results and discussion

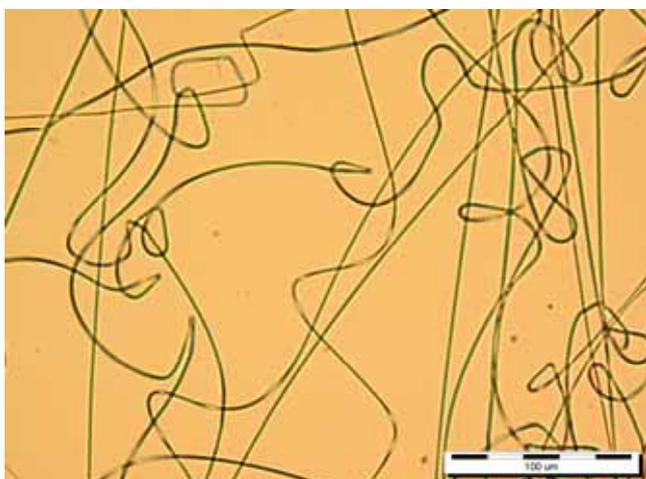
The average diameters of the electrospun fibers which were investigated by an optical microscope ranged from 1.14 to 2.93  $\mu\text{m}$ . However, it was observed that some fibers had a diameter smaller than 200 nm and they were visible only by SEM images. The images showed that, in some cases, the fibers tended to stay close to each other. Probably, the main reason for this was the insufficient working distance  $h$ . All the formed fibers were mainly straight at lower voltages of 16 kV and 20kV (Fig.5). Oppositely, the electrospun fibers started to remain whipped while increasing the applied voltages from 24 to 30kV (Fig.6). The whipped fiber structure was also noted when reducing the flow rate (Fig.7).



**Figure 5.** Optical microscopy image of the PVB fibers with 3 wt.% modified SiO<sub>2</sub> nanoparticles ( $Q = 1\text{ mL/h}$ ,  $V = 20\text{ kV}$ ,  $h = 10\text{ cm}$ )



**Figure 6.** Optical microscopy image of the PVB fibers with 3 wt.% unmodified SiO<sub>2</sub> nanoparticles ( $Q = 1\text{ mL/h}$ ,  $V = 24\text{ kV}$ ,  $h = 10\text{ cm}$ )



**Figure 7.** Optical microscopy image of the PVB fibers ( $Q=0.4\text{ mL/h}$ ,  $V=20\text{ kV}$ ,  $h=10\text{ cm}$ )

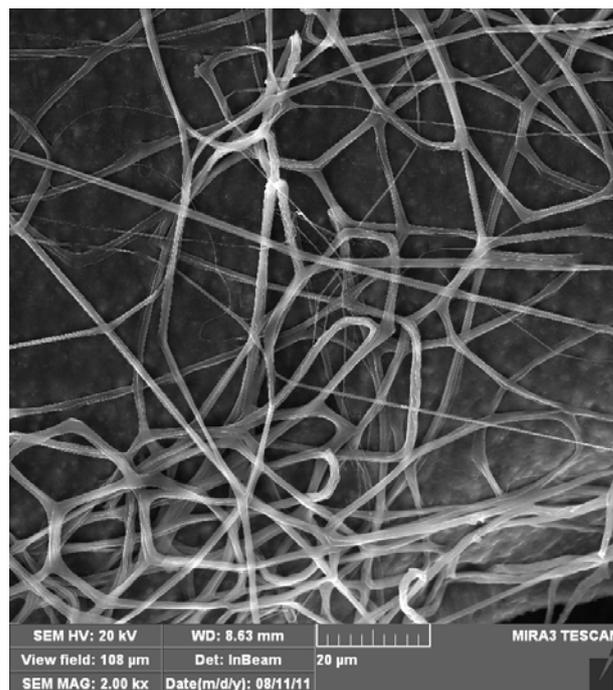
The fibers of the PVB solution showed an expected tendency of decreasing their diameters at increasing the applied voltages (Table 1). The maximum value of an average fiber diameter is produced with  $Q = 1\text{ mL/h}$ ,  $V = 20\text{ kV}$ , and the minimum one is obtained by  $Q = 0.8\text{ mL/h}$ ,  $V = 20\text{ kV}$  process parameters.

**Table 1.** Average fiber diameters of the PVB solution with different process parameters

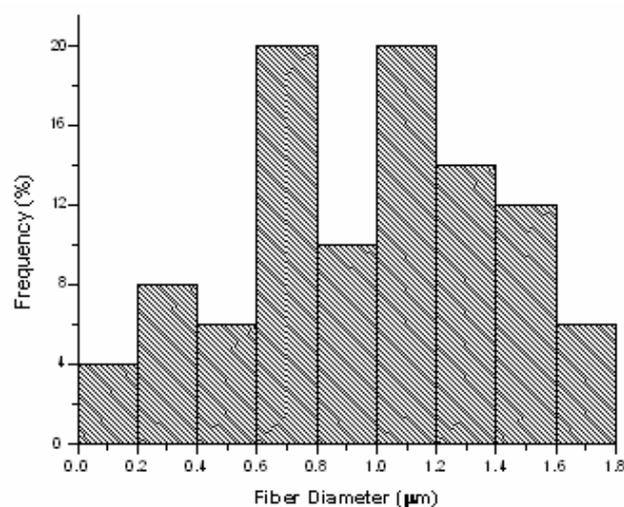
PVB solution		
Flow rate	Applied voltage	Average diameter
$Q$ , mL/h	$V$ , kV	$d_{avg}$ , $\mu\text{m}$
0.2	20	1.67
0.4	20	1.68
0.6	20	1.54
0.8	20	1.46
1	16	2.13
1	20	2.94
1	24	2.08
1	28	1.88
1	30	1.77

However, the SEM images showed fibers of smaller size, with the diameters within the nanoscale range (Fig.8). For example, some of the observed PVB fibers had diameters smaller than 200 nm during their analysis in the Image Pro

Plus software. The appropriate histogram of the fiber diameter distribution was the result of this analysis (Fig.9).



**Figure 8.** SEM image of the PVB fibers ( $Q=1\text{ mL/h}$ ,  $V=30\text{ kV}$ ,  $h=10\text{ cm}$ )



**Figure 9.** Histogram of the fiber diameter distribution of the PVB fibers ( $Q = 1\text{ mL/h}$ ,  $V = 30\text{ kV}$ ,  $h = 10\text{ cm}$ )

The appropriate modification of the silica particles by AMEO silane assumes hydrolysis of  $\gamma$ -aminopropyltriethoxysilane ( $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_3\text{H}_6\text{NH}_2$ ) by the loss of alkoxy groups which provides chemical reaction with the hydroxyl groups at the silica surface, [7]. According to the images obtained by optical microscopy, the diameters of the fibers with the SiO<sub>2</sub> nanoparticles were of similar size comparing to the neat PVB fibers. These diameters, all with different concentrations of silica nanoparticles, were not significantly affected either by the applied voltage or by the flow rate. Based on the SEM images of the fibers with unmodified nanoparticles, it was evident that these nanoparticles fused into big aggregates (Fig.10). Unlike them, the modified nanoparticles were well-distributed inside the fibers, and did not agglomerate to a great extent (Fig.11).

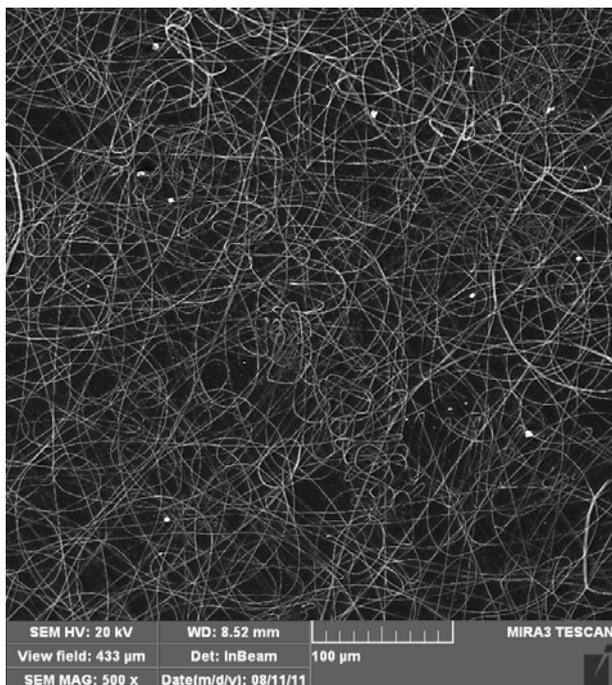


Figure 10 - SEM photograph of the PVB fibers with 1 wt.% unmodified SiO<sub>2</sub> nanoparticles (Q = 1 mL/h, V = 30 kV, h = 10 cm)

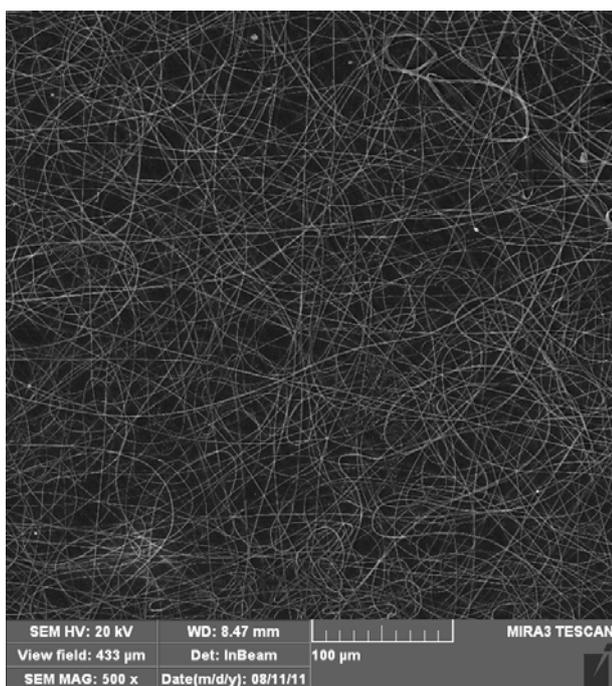


Figure 11 - SEM photograph of the PVB fibers with 1 wt.% modified SiO<sub>2</sub> nanoparticles (Q = 1 mL/h, V = 30 kV, h = 10 cm)

## Conclusion

The morphology of the electrospun PVB-SiO<sub>2</sub> composite fibers was investigated by changing two process parameters - the flow rate of the solution  $Q$  and the applied voltage  $V$ . The produced nanofibers were merely narrow at low voltages of 16 kV and 20 kV. However, the fibers began to coil at the voltage of 24 kV and by further increasing, up to 30 kV, they were completely whipped. The modification of the silica surface with AMEO silane leads to a better dispersion and deagglomeration of the SiO<sub>2</sub> nanoparticles inside the PVB fibers.

## Acknowledgements

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## References

- [1] RENEKER, D.H., CHUN, I.: *Nanometre diameter fibers of polymer, produced by electrospinning*, *Nanotechnology*, 7, 1996, pp.216-223.
- [2] SILL, T.J., VON RECUM, H.A.: *Electrospinning: Applications in drug delivery and tissue engineering*, *Biomaterials*, 29, 2008, pp.1989-2006.
- [3] ZHANG, C., YUAN, X., WU, L., HAN, Y., SHENG, J.: *Study on morphology of electrospun poly(vinyl alcohol) mats*, *European Polymer Journal*, 41, 2005, pp.423-432.
- [4] GARG, K., BOWLIN, G.L.: *Electrospinning jets and nanofibrous structures*, *BIOMICROFLUIDS*, 5, 2011, art. No.013403.
- [5] MOGHE, A.K.: Ph. D. Dissertation, Raleigh, North Carolina, 2008.
- [6] SCHUEREN, L.V., SCHOENMAKER, B.D., KALAOGLU, O.I., CLERCK, K.D.: *An alternative solvent system for the steady state electrospinning of polycaprolactone*, *European Polymer Journal*, 47, 2011, pp.1256-1263.
- [7] TORKI, A.M., STOJANOVIĆ, D.B., ŽIVKOVIĆ, I.D., MARINKOVIĆ, A., ŠKAPIN, S.D., USKOKOVIĆ, P.S., ALEKSIĆ, R.R.: *The Viscoelastic Properties of Modified Thermoplastic Impregnated Multi-axial Aramid Fabrics*, *Polymer Composites*, 33, 2012, pp.158-168.

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# Analiza formiranja PVB-SiO<sub>2</sub> nanokompozitnih vlakana pomoću elektrospining procesa

Poli (vinil butiral)-silika (PVB-SiO<sub>2</sub>) nanovlakna su dobijena metodom elektrospininga. Eksperimenti su izvedeni u rastvoru 10 mas.% PVB-a u etanolu koji je korišćen kao rastvarač. Nanočestice silike su dodate sa različitim sadržajem od 1, 3 i 5 mas.% SiO<sub>2</sub> i modifikovane  $\gamma$ -aminopropiltrioksi silanom (AMEO silanom). Istražen je uticaj procesnih parametara elektrospininga na nanokompozitna vlakna PVB-SiO<sub>2</sub>. Struktura PVB-SiO<sub>2</sub> nanokompozitnih vlakana je proučavana pomoću optičke mikroskopije i skenirajuće elektronske mikroskopije (SEM). Morfologija proizvedenih nanokompozitnih vlakana i njihova raspodela je analizirana u Image Pro Plus softveru.

**Ključne reči:** nanovlakna, nanokompozitna vlakna, nanočestice, aminopropiltrioksi silan (AMED silan), polivinilbutiral silika (PVB-SiO<sub>2</sub>), elektrospining metoda, eksperimentalni rezultati.

## Анализ формирования пвб-SiO<sub>2</sub> нанокompозитных волокон с помощью электрoкрутящихся процессов

Нановолокна поли(винилового бутирала) диоксида кремния (SiO<sub>2</sub>-ПВБ) были получены с использованием электрoкрутящихся методов. Эксперименты проводились в растворе 10 % массы ПВБ в этаноле, которому были добавлены наночастицы кремния с различными содержаниями 1, 3 и 5 % массы SiO<sub>2</sub>. Наночастицы кремния были немодифицированные и изменены  $\gamma$ -аминопропилтриэтоксидиланом (АМЕО силаном). Исследовано влияние технологических электрoкрутящихся параметров на композитные волокна ПВБ-SiO<sub>2</sub>. Структура ПВБ-SiO<sub>2</sub> нанокompозитных волокон была исследована с помощью оптической микроскопии и сканирующей электронной микроскопии (SEM). Морфология производства нанокompозитных волокон и их распределение анализируются при помощи Image Pro Plus программного обеспечения.

*Ключевые слова:* нановолокна, нанокompозитные волокна, наночастицы, аминопропилтриэтоксидилан (АМЕО силан), поливинилбутирал диоксида кремния (ПВБ-SiO<sub>2</sub>), электрoкрутящиеся методы, экспериментальные результаты.

## Analyse de la formation des fibres nano composites par le processus d'électrofilage

Les nano fibres (polyvinylebutyral silice) PVB-SiO<sub>2</sub> ont été obtenus par la méthode d'électrofilage. Les essais ont été faits avec la solution de 10% mas PVB dans l'éthanol où on a ajouté les nano particules de silice avec les différents contenus de 1,3 et 5 % mas de SiO<sub>2</sub>. Les nano particules de silice ont été non modifiées et modifiées à l'aide de  $\gamma$ -aminopropyletriéthoxy silane (AMEO silane). On a étudié l'influence des paramètres du processus d'électrofilage sur les fibres composites PVB-SiO<sub>2</sub>. La structure PVB-SiO<sub>2</sub> des fibres nano composites a été étudiée au moyen des la microscope optique et la microscopie scannée. La morphologie des fibres nano composites produites et leur distribution sont analysées par le logiciel Pro Plus.

*Mots clés:* nano fibres, nano fibres composites, nano particules, aminopropyletriéthoxy silane (AMEO silane), polyvinylebutyrale silice (PVB-SiO<sub>2</sub>), méthode d'électrofilage, résultats expérimentaux.