Electrospun Poly(vinylbutyral)/silica Composite Fibres for Impregnation of Aramid Fabrics

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The poly (vinyl butyral)/silica (PVB/SiO_2) composite fibers were produced by the electrospinning process. The experiments were performed with the PVB solution in concentration of 10 wt.% where ethanol was used as the solvent. The silica nanoparticles were added into the solution in different content of 1, 3 and 5 wt.% SiO_2. The PVB fibers with 50 wt.% SiO_2 nanoparticles were deposited on p-aramid fabrics which were coated with PVB solution. The effect of the processing parameters on the morphology of PVB/SiO_2 composite fibers was analysed. Mechanical properties of the p-aramid fabrics were tested by dynamic mechanical analysis (DMA).

Keywords: electrospinning, electrospun composite fibers, silica nanoparticles, p-aramid fabrics

Electrospinning is a simple and unique technology for producing polymer fibers from polymer solutions and polymer melts. The produced fibers are in the micrometre and nanometre scale diameters [1]. The process of electrospinning is driven by a high voltage source to charge the polymer solution. These free charges are on the surface or inside a polymer liquid. The liquid is then accelerated toward a grounded metal collector of opposite polarity. The travel of polymer jet allows the solvent to evaporate from it and leads to the deposition of the solid polymer fibers on the collector. In fact, as the jet moves towards the collector, the electrostatic forces accelerate and stretch the jet. Stretching and evaporation of the solvent cause the jet diameter to become smaller. The basic electrospinning set-up consists of a syringe filled with the polymer solution, needle, a high voltage source and a grounded conductive collector [2]. An electric field is initiated between the tip of a syringe and the collector, and, thus, 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. When these forces overcome the surface tension of the polymer solution, a jet is ejected from the tip of the syringe. Then, the solvent from the jet evaporates leading to the randomly oriented fibers on the collector [3-5].

Poly (vinyl butyral) is a nontoxic and odourless polymer which is often used as a mesopore template. Because of its good compatibility with inorganic materials, PVB is a common component for producing of organic-inorganic hybrid composites [6]. Chen *et al.* [7] investigated the PVB/silica fibers obtained from the PVB/silica precursor where PVB acted as the fiber template. The PVB/silica solutions at different ratios were tested. It was observed that no fiber was obtained when the ratio was 5%. With increasing this ratio, bead-on-string structures appeared, but, with further increasing, the beads dissappeared and the smooth fibers were produced when the ratio was 20%. It was concluded that the high PVB concentration was a key factor in preparing smooth fibers. Another study with the multiwalled carbon nanotube (MWCNT)/PVB composite fibers is reported by Imaizumi *et al.* [8]. In this research the fibers were prepared by electrospinning, successive twisting and heat treatment. The addition of MWCNT enhanced the mechanical properties of the composite fibers. According to the study by Svrcinova *et al.* [9], ethanol and methanol as the solvents of PVB were suitable for electrospinning and fiber forming unlike butanol and isopropanol. Thus, 10 wt.% PVB-ethanol solution mixed with neat silica nanoparticles was used in our study.

Electrospinning parameters and concentrations of silica nanoparticles were varied in order to investigate their influence on the fiber morphology.

Aramid (Twaron and Kevlar) fibers represent PPTA (poly (paraphenylene terephthalamide)). The fibers consist of aramid crystal structure along the chain direction, and the chains are linked by the hydrogen bonds in a particular direction. The van der Waals bonds exist between the planes formed by hydrogen-bonded chains [10].

Para-aramid (*p*-aramid) fibers are developed to deliver high performance with following properties: high operating temperature and heat resistance, low flammability, high chemical resistance (with the exception of a few strong acids and alkalis), good stability within a wide range of temperatures over longer periods of time, high tensile strength and elasticity modulus and good strength to density ratio [11]. The use of multiple layers of woven *p*-aramid fabric provides protection from fragmenting munitions and explosive devices [12]. Besides their ballistic applications for bullet-proof vests, helmets and vehicle armouring, they can be used for protection of telecommunication cables, containers in the transport industry, pipes and tanks in plant engineering, etc. [11].

The modern flexible armor is made mainly from shear thickening fluid (STF)-Kevlar composites, where STF is impregnated into the Kevlar fabrics. STF represents the suspension of about 55 wt.% silica in polyethylene glycol (PEG) [13], or the product of dispersing 52% - 57% vol. colloidal silica particles in 200 Mw PEG [14, 15]. According to these results, in this study, the PVB composite fibers with 50 wt.% SiO_2 nanoparticles were deposited on *p*-aramid fabrics which had been impregnated with the PVB solution.

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Experimental part

Materials and methods

A powder poly (vinyl butyral) (Mowital B75H, Kuraray Specialities Europe) and absolute ethanol (Zorka Pharma, Šabac) were used for preparing the PVB solution (10 wt.%). The silica nanoparticles with an average particle diameter of about 7 nm were obtained from Evonik-Degussa, Aerosil 380. Multiaxial aramid fabrics with *p*-aramid fiber type were received from Martin Ballistic Mat, Ultratex, Serbia.

The silica nanoparticles were put into the PVB solution (10 wt.% in ethanol) and stirred continuously for 24 h, and ultrasonically dispersed for 15 min afterwards. The PVB solutions with and without the silica particles were electrospun by varying applied voltages and flow rates. The electrospinning apparatus used for the experiments in this work is Electrospinner CH-01 (Linari Engineering). A set of experiments was driven with the applied voltages of 16, 20, 24, 28 and 30 kV while the flow rate was kept constant at Q = 1 mL/h. Another experimental set was performed with flow rates valued 0.2, 0.4, 0.6 and 0.8 mL/h while the voltage was held at V = 20 kV. During the electrospinning process, the formed fibers were deposited onto the flat aluminium foil which served as a collector. The distance beetwen the needle tip and the collector was h = 10 cm in all cases.

The schematic drawing of the electrospinning process along with electrospinning set-up is depicted in figure 1(a). The innovative idea for the electrospun fibers was their deposition onto the aramid fabrics. Three pieces of *p*-aramid fabrics were coated with the PVB solution and the produced PVB-SiO_2 composite fibers with 50 wt.% silica nanoparticles were deposited continuously onto the fabrics during the electrospinning process (fig. 1(b)). The dimension of each fabric was 29.7 cm x 21 cm, weighing 40 g approximately. The flow rate of the PVB-SiO_2 solution for this process was Q=50 mL/h and the voltage was held at V=30 kV. The *p*-aramid fabrics with the deposited PVB-SiO_2 composite fibers were hot compressed using N 840 D Hix Digital Press (Hix, Corp., USA) at a temperature of 170°C for 30 min under pressure of 4 bar. The fabrics were additionally pressed with P-125 press (170°C, 10.6 MPa) for 2 h and then brought under pressure of 20.6 MPa for 1 h.

The functional groups of fiber mats were analysed by attenuated total reflection FTIR (ATR–FTIR) spectroscopy. The FTIR spectrometer was joined to an ATR model Smart Orbit Nicolet 5700. Thirty-two scans with 4 cm^{-1} resolution were carried out for each sample in the reflection mode.

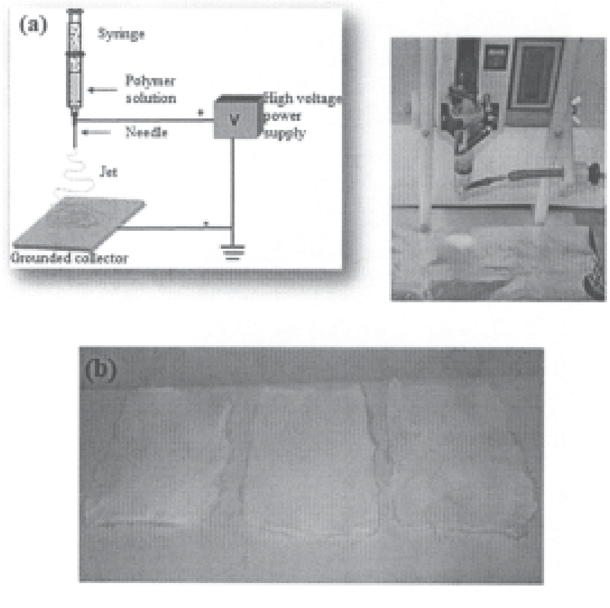

Fig. 1. Electrospinning process: (a) Basic electrospinning set-up; (b) Coated *p*-aramid fabric with electrospun PVB-SiO_2 composite fibers

The thermal properties of fiber mats were examined in a nitrogen atmosphere from the room temperature to 150°C at a heating rate of 10 °C/min using a differential scanning calorimeter (DSC, Q10 TA Instruments, USA). Samples (10 mg) were hermetically sealed in an aluminum pan, put in the DSC cell together with an empty aluminum pan as the reference material, and heated with a continuous nitrogen flow of 50 mL/min.

Dynamic mechanical analysis (DMA, Q800 TA Instruments, USA) for the *p*-aramid fabrics was conducted in a dual cantilever mode at a frequency of 1 Hz where the temperature ranged from 30 to 170 °C with a heating rate of 3°C/min for the evaluation of the storage modulus (E') and Tan Delta (tan δ).

The morphology of obtained fibers was investigated both by optical microscope OLYMPUS CX41 and scanning electron microscopy (SEM) on a MIRA3 TESCAN electron microscope at 20 kV. The average diameters of the electrospun fibers were measured and calculated by Image-Pro Plus analysis.

Results and discussions

FTIR analysis

FTIR analysis of the PVB fiber mats (fig. 2(a)) showed the presence of OH groups at 3445 cm^{-1}. The peaks around 2920 cm^{-1} and 2870 cm^{-1} belonged to CH groups stretching vibrations, and the peak at 993 cm^{-1} was referred to the C-OH vibration. C=O groups from PVB corresponded to the peak at 1736 cm^{-1}. The peak at 2936 cm^{-1} and 2874 cm^{-1} which originated from PVB decreased with the addition of 5 wt.% SiO_2 nanoparticles (fig. 2(b)). The peak at 1088 cm^{-1} referred to Si-O-Si stretching vibrations originated from the silica nanoparticles.

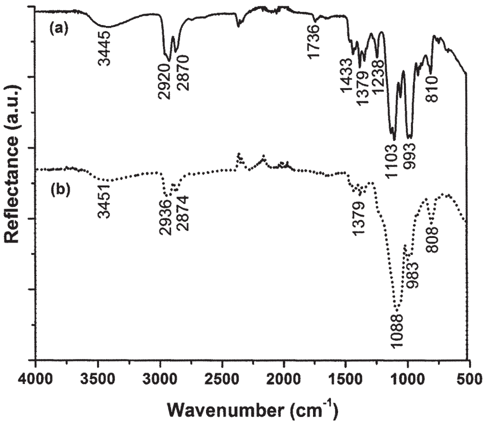

Fig. 2. FTIR analysis of the electrospun mats: (a) PVB; (b) PVB with 5 wt.% SiO_2 nanoparticles

Differential Scanning Calorimetry (DSC)

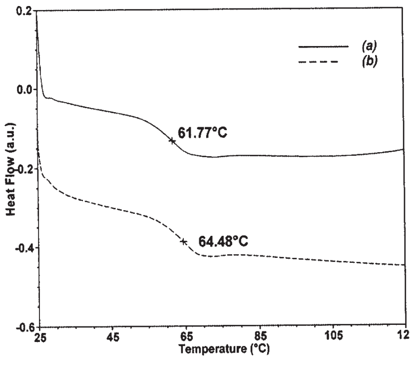

Fig. 3. DSC traces of different kinds of PVB fiber mats: (a) PVB in ethanol; (b) PVB with 5 wt.% silica nanoparticles

PVB fiber									
Flow rate Q [mL/h]	0.2	0.4	0.6	0.8	1	1	1	1	1
Applied voltage V [kV]	20	20	20	20	16	20	24	28	30
Average diameter d_{avg} [μm]	1.67	1.68	1.54	1.46	2.13	2.94	2.08	1.88	1.77
Standard deviation [μm]	0.07	0.06	0.04	0.03	0.07	0.11	0.04	0.03	0.06

Table 1
AVERAGE PVB FIBER DIAMETERS WITH DIFFERENT PROCESS PARAMETERS

The glass transition temperature (T_g) of the PVB powder, Mowital B75H, is ≈ 74 °C [14]. However, the glass transition temperature of PVB fibers when ethanol was used as a solvent was about 62 °C, which was probably caused by residue ethanol while this temperature was about 64.5 °C for the PVB fibers with 5 wt.% silica nanoparticles (fig. 3). The cause of the increase of T_g for PVB fibers with nanoparticles was probably due to the formation of hydrogen bonds between polymer chains and surfaces of the nanoparticles.

Fiber dimension and morphology

The average diameters of electrospun fibers from the optical microscopy images ranged from 1.14 to 2.93 μm. The diameter of some fibers was smaller than 500 nm, which could be visible only by the SEM images.

The PVB fibers showed an expected tendency of decreasing their diameters with increasing the applied voltages (table 1). The analysis of fiber diameter by using the optical images were, beside the table 1, illustrated in 3D graph (fig. 4(a)). The maximam value of the average fiber diameter was produced with Q = 1 mL/h and V = 20 kV, and the minimum one was obtained by Q = 0.8 mL/h and V = 30 kV. According to the images obtained by optical microscopy, the diameters of the fibers with the SiO_2 nanoparticles were of similar size. These diameters were not significantly affected either by the applied voltage or by the flow rate.

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 narrow at lower voltages of 16 kV and 20 kV (fig. 4(b) and 4(c)). Oppositely, the electrospun fibers started to remain whipped while increasing the applied voltages from 24 to 30 kV (fig. 4(d)). The whipped fiber structure was also obtained with reducing the flow rate (fig. 4(e)).

However, the SEM images showed thin fibers with diameters within the nanoscale range. The histogram of the fiber diameter distribution showed that most of the PVB fibers were in diameter beetwen 0.7-0.8 μm (fig. 5(a)).

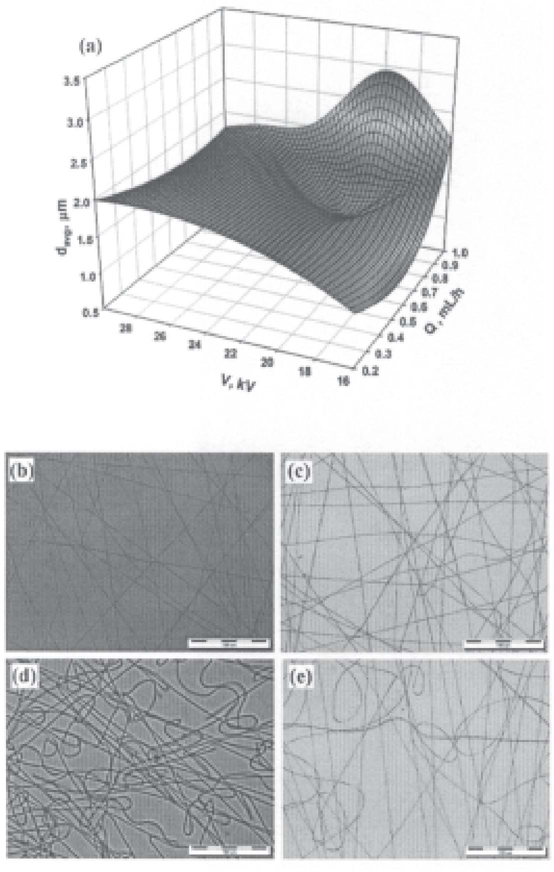

Fig. 4. Optical image results: (a) 3D chart of the data in table 1; Optical microscopy images of the PVB fibers (scale bar 100 m): (b) with 5 wt.% SiO_2 nanoparticles (Q = 1 mL/h, V = 20 kV, h = 10 cm); (c) with 1 wt.% SiO_2 nanoparticles (Q = 1 mL/h, V = 16 kV, h = 10 cm); (d) (Q = 1 mL/h, V = 24 kV, h = 10 cm); (e) with 1 wt.% SiO_2 nanoparticles (Q = 0.8 mL/h, V = 20 kV, h = 10 cm)

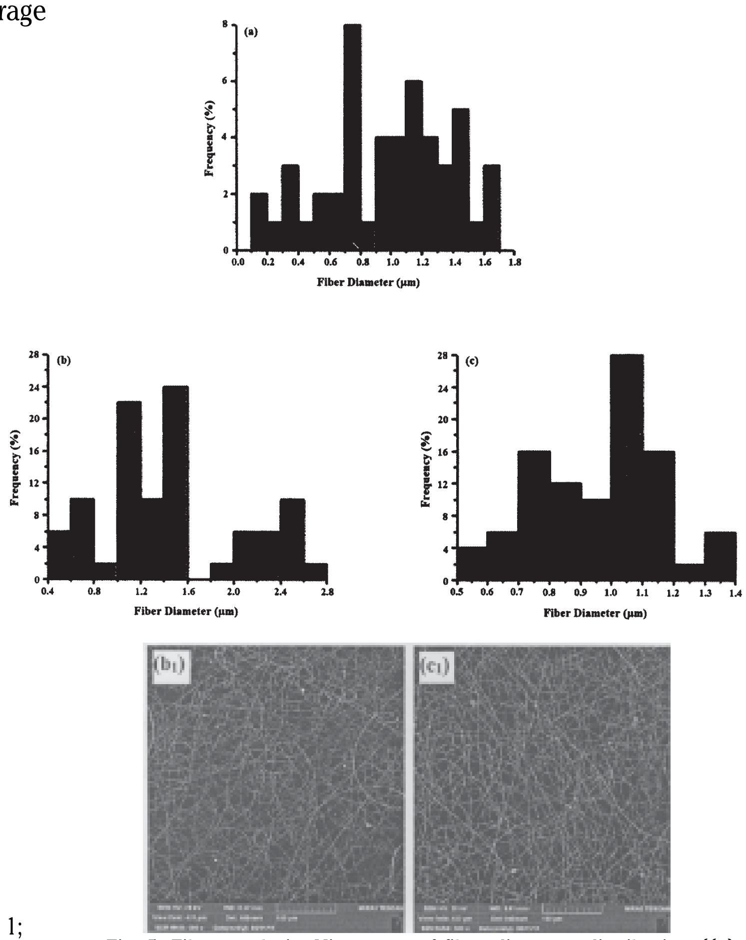

Fig. 5. Fiber analysis: Histogram of fiber diameter distribution ((a) PVB fibers; (b) PVB fibers with 1 wt.% SiO_2 nanoparticles; (c) PVB fibers with 5 wt.% SiO_2 nanoparticles) ; SEM photographs of the PVB fibers (scalebar 100 μm, Q = 1 mL/h, V = 30 kV, h = 10 cm): (b1) with 1 wt.% SiO_2 nanoparticles; (c1) with 5 wt.% SiO_2 nanoparticles

Table 2
DMA RESULTS FOR *p*-ARAMID FABRICS

Sample	E' (MPa) at 40 °C	E' (MPa) at 70 °C	T_g (°C)	*tan δ*
p-aramid/PVB	2230	567	68.6	0.37
p-aramid/PVB/PVB 50 wt. SiO_2 fibers	2336	1355	76.4	0.36

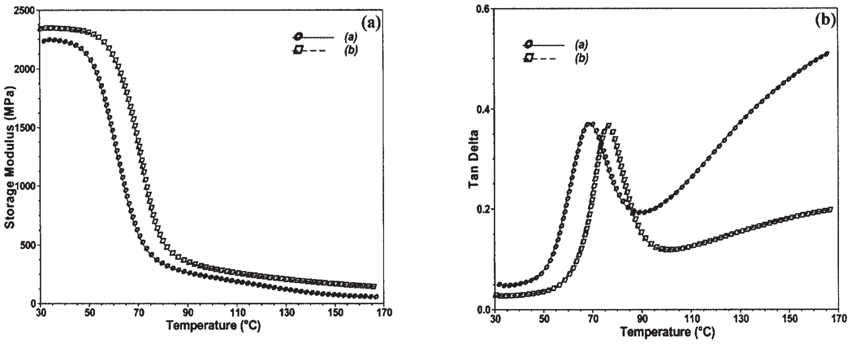

Fig. 6. DMA curves: (a) Storage modulus vs. temperature ((a) *p*-aramid/PVB fabrics and (b) *p*-aramid/PVB fabrics with PVB composite fibers); (b) Tan Delta vs. temperature ((a) *p*-aramid/PVB fabrics and (b) *p*-aramid/PVB fabrics with PVB composite fibers)

The SEM images of PVB fibers with 1wt.% SiO_2 nanoparticles (fig. 5(b1)) showed that the analysed fiber diameters were within the range 0.4-2.8 μm (fig. 5(b)). The SEM photographs of the electrospun PVB fibers with 5 wt.% SiO_2 nanoparticles (fig. 5(c1)) depicted that majority of these fibers were between 1μm and 1.1 μm in diameters (fig. 5(c)). The experimental conditions for the above mentioned fibers were Q = 1 mL/h, V = 30 kV and h = 10 cm.

Based on the SEM images of the fibers with nanoparticles, it was evident that with increasing the concentration of the silica nanoparticles, they fused into aggregates (figs. 5(b1) and 5(c1)).

Preliminary results of the dynamic mechanical analysis (DMA)

According to the studies [13-15], the PVB composite fibers with 50 wt.% SiO_2 nanoparticles were deposited on *p*-aramid fabrics which had been impregnated with the PVB solution. Figure 6(a) showed the temperature dependence of the storage modulus of the *p*-aramid fabric with PVB film and the *p*-aramid fabric with PVB/PVB-50 wt.% SiO_2 fibers. The composite *p*-aramid/PVB showed a lower value of the storage modulus at the temperatures of 40 and 70 °C. The difference in the two storage moduli was greater with increasing the temperature (table 2). The glass transition temperature of the *p*-aramid/PVB/PVB-50 wt.% SiO_2 fibers composite was 76.4 °C, about 8 °C higher that the *p*-aramid/PVB composite (table 2). Tan Delta of the *p*-aramid/PVB/PVB-50 wt.% SiO_2 fibers composite had a lower value which indicated that the addition of the PVB fibers with silica nanoparticles enhance thermal properties of the *p*-aramid fabrics (table 2, fig. 6(b)). The mechanical properties were slightly improved, but insufficiently due to the weak bonds among *p*-aramid fabric, PVB, and silica nanoparticles.

The addition of the silica nanoparticles enhanced thermal properties of the composite fibers. The future research into the PVB fibers with SiO_2 nanoparticles deposited on *p*-aramid fabrics will be focused on their application in antiballistic protection.

Conclusions

The effects of flow rate of the solution Q, the applied voltage V, the nanoparticle content and treatment on the structure and morphology of electrospun PVB/SiO_2 composite fibers were investigated. The produced fibers were merely narrow at low voltages of 16 kV and 20 kV. However, the fibers began to whip at the voltage of 24 kV, and, by further increasing the applied voltage up to 30 kV, they were completely coiled.

The addition of silica nanoparticles into PVB fibers enhanced thermal properties of the *p*-aramid fabrics comparing to ones coated with PVB film. The next step will be a modification of *p*-aramid surface or silica nanoparticles in order to achieve better bonds among the components and improve mechanical properties of the composite.

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