

Rheology of Poly(vinyl butyral) Solution Containing Fumed Silica in Correlation with Electrospinning

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Abstract The rheological properties in question are influenced by many factors, ranging from the characteristics of the given polymer or solvent to the flowing conditions. The primary focus of this study is to analyse the rheological behaviour of poly(vinyl butyral)—Mowital B 60H—(PVB) solutions dissolved in methanol and a blend of these with fumed silica nanoparticles. The preparation of the nanofibrous web and the quality of nanofibres were correlated with the rheology of the polymer solution. It was discerned that drastically intensifying shear viscosity and the elasticity of the solution exerted a negligible effect on the formation of fibres, a finding which has rarely been discussed in the literature. The morphologies and structures of the PVB/silica nanofibrous membranes were investigated by scanning electron microscopy, thermogravimetric analysis and Fourier transform infrared spectroscopy.

Keywords Electrospinning; Nanofibres; Poly(vinyl butyral); Fumed silica; Rheology

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INTRODUCTION

Electrospinning is a process for producing a nanofibrous web, as applied in areas such as nanocomposites^[1], biomedical engineering^[2, 3], sensors and superhydrophobic membranes^[4]. The fibres are formed in the presence of an electric field, wherein the charged, streaming fluid jet of the polymer solution travels towards the grounded collector. During transit, the diameter of the jet is drawing, stretched by high elongation and shear stresses at solvent evaporation. A number of parameters act on the fluid jet, tending to break it into small droplets. Indeed, a great many such parameters have been extensively studied in the literature^[5–8]. Nevertheless, some authors claim that the diameter of the nanofibres is solely dependent on the properties of the solution^[9, 10].

Extensive research on polymers that possess the capacity to be spun into fibres has revealed that optimal conditions vary depending on the given polymer. In particular, the properties of the solution and any associated rheological behaviour patterns are the main factors affecting initiation of the jet, its continuation and, ultimately, formation of the fibres. Such rheological characteristics are influenced by polymer type, concentration, the quality of the solvent and the additives utilized. For example, hydrophobic fumed silica (if used as an

additive) flocculates and forms gel; hence, the viscosity and elasticity of the polymer solution can be drastically altered, which can be manifested in both fibre morphology and overall solution spinnability. Dufficy *et al.*^[11] compared rheological trends in PAN/DMF solutions containing fumed silica particles with the electrospun fibre morphology.

Polymer/silica fibrous nanocomposites have the ability to enhance mechanical and thermal properties. In addition, the presence of silica can increase or decrease hydrophobicity^[11] or improve catalytic activities^[12]. Fumed silica is an amorphous silicon dioxide with the potential to comprise fine particles of approximately 8–20 nm, and it can be easily mixed with a spinnable polymer solution. For instance, Xu *et al.*^[13] prepared nanofibres with controlled wettability using poly(vinyl butyral) (PVB) and fumed silica. Moreover, Chen *et al.*^[14] studied the synthesis and characterization of PVB/silica nanofibres, utilizing X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy and energy dispersive spectroscopy. Nevertheless, the rheological parameters of PVB/silica solutions have rarely been investigated.

In this context, this work explores rheological properties by measuring them in steady and oscillatory modes. Of particular interest are the drastic differences found between the shear viscosity and elasticity of neat PVB solutions and PVB/silica solutions. Furthermore, an attempt was made to correlate the quality of the fibres with their rheological parameters. In terms of analysis, the presence of silica in the

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nanofibrous membrane was detected on a thermogravimetric analyser and a Fourier transform infrared spectrometer.

EXPERIMENTAL

Materials

Poly(vinyl butyral) ($M_w = 6 \times 10^4$ g/mol; Mowital B 60H; kindly provided by Kuraray Specialties Europe) was dissolved in methanol (PENTA; quality of p.a.) at different concentrations. The structure of Mowital B 60H comprises vinyl butyral, vinyl alcohol and vinyl acetate, herein at 75%–81%, 18%–21% and 1%–4%, respectively. Fumed silica particles with the surface modification of Aerosil R 805 (octyl = $(O_3)-Si-C_8H_{17}$) were generously provided by the Evonik Degussa Corporation (Germany). The size of the individual particles equalled 10–12 nm, with a large surface area (125–175 m²/g). In order to homogenize neat PVB solutions and PVB/silica blends, a magnetic stirrer was utilized at 250 r/min at 25 °C over 48 h. All the chemicals were used as received without further purification and were mixed together in one step. In all cases, the amount of silica nanoparticles is relative to entire solutions.

Characterization of the Polymer Solution

Rotational and oscillatory rheological measurements were performed on a Physica MCR 501 device (Anton Paar, Austria), equipped with concentric cylinders (26.6/28.9 mm inner/outer diameters) at a constant temperature of 25 °C. The shear rate applied when taking the rotational measurements ranged from 0.01 s⁻¹ to 300 s⁻¹. The oscillatory tests were performed at an amplitude within the linear region (strain = 1%), at a frequency of 0.1–100 s⁻¹.

The conductivity of the PVB solutions was measured on a Conductivity Meter Lab 960 device (SCHOTT Instruments, Germany). Meanwhile, surface tension was determined *via* the Wilhelmy plate method (10 mm × 19.9 mm × 0.2 mm), using a Krüss K 100 force tensiometer (Krüss, GmbH Germany).

Electrospinning of the Polymer Solutions

The nanofibrous webs were spun on a laboratory device that consisted of a high voltage power supply (Spellman SL70PN150, USA), a carbon steel stick (10 mm in diameter) and a motionless flat metal collector. The electrospinning process was carried out at a voltage of 25 kV, while the tip-to-collector distance was set to 100 mm under ambient conditions (temperature (23 ± 1) °C, relative humidity (32 ± 1)%). The drop of polymer solution placed onto the tip measured approximately 0.2 mL.

Characterization of the Nanofibrous Web

Characterizing the fibres involved using a Vega 3 high resolution scanning electron microscope (Tescan, Czech Republic). Prior to imaging, a conductive layer was sputtered onto the samples. The mean diameter of the fibres was determined with the aid of Adobe Creative Suite software, in which 300 fibres were analysed from 3 different images.

Thermogravimetric analysis was performed on a TGA Q500 thermogravimeter (TA Instruments, USA). Measurements were performed in a nitrogen atmosphere at the flow rate of

50 mL/min with temperature ranging 25–800 °C. A typical heating rate of 10 K/min was applied. The sample weight equalled 7 mg to 9 mg.

Fourier transform infrared spectroscopy (FTIR) was also used to characterize the prepared fibres, the device having been set to attenuated total reflection (ATR) mode and fitted with a diamond crystal. Measurement conditions included 64 scans at the resolution of 2 cm⁻¹ and the range of 4000–400 cm⁻¹. Analysis was carried out on Nicolet 6700 spectrometer (ThermoFisher Scientific, USA).

RESULTS AND DISCUSSION

The Effect of Polymer Concentration on Electrospinning

Conductivity and surface tension were determined to discern the effect exerted by the properties of the solution on the morphology of the fibres, as shown in Fig. 1. According to Fong *et al.*^[15], the surface tension of the polymer solution is influenced by the solvent and the solvent mixture. The surface tension values for the neat PVB and PVB/silica solutions did not change significantly by increasing the concentration of PVB. However, the conductivity of both samples rose with further concentration of PVB. The ion concentration of the PVB solution, hence also its polarity, increased as a consequence of greater concentration of the polymer^[16]. As the fumed silica had a minimal effect on surface tension and conductivity, their influences on the fibre formation in this particular polymer-solvent system were insignificant.

In the first instance, rotational tests were performed to determine the shear viscosity of the solutions as a function of shear rate. Comparison of the neat PVB solution and

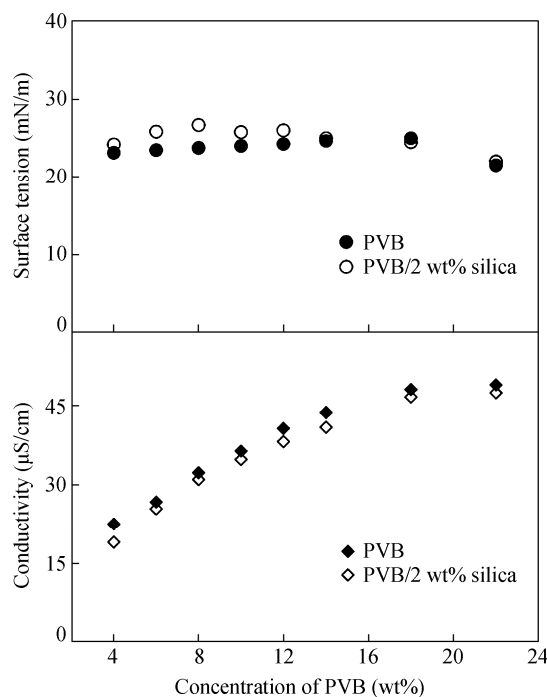


Fig. 1 The surface tension and conductivity of neat PVB and PVB/2 wt% silica solutions as dependence on the concentration of PVB

PVB/silica mix is depicted in Fig. 2. As expected, shear viscosity increases alongside higher concentration of the neat polymer. The shapes of the viscosity curves clearly highlight the completely different types of fluid utilized herein, indicating Newtonian and non-Newtonian behaviour. In the case of the neat PVB solution, viscosity is constant up to high shear rates. In contrast, all the PVB/silica solutions exhibit diminishing viscosity values in parallel with increase in shear rate, *i.e.* shear-thinning behaviour. These findings lead to the conclusion that the pseudo plasticity of PVB/silica solutions relates to the occurrence of particle-polymer interaction in the solutions. The fumed silica itself causes networks and aggregates to form between each individual molecule. During the shear process, the network between the polymer molecules and silica NPs is destroyed, while the molecules are oriented parallel to the direction of said shear, resulting in reduced viscosity. This means that viscosities of both types of the solutions share similar values at high shear rates.

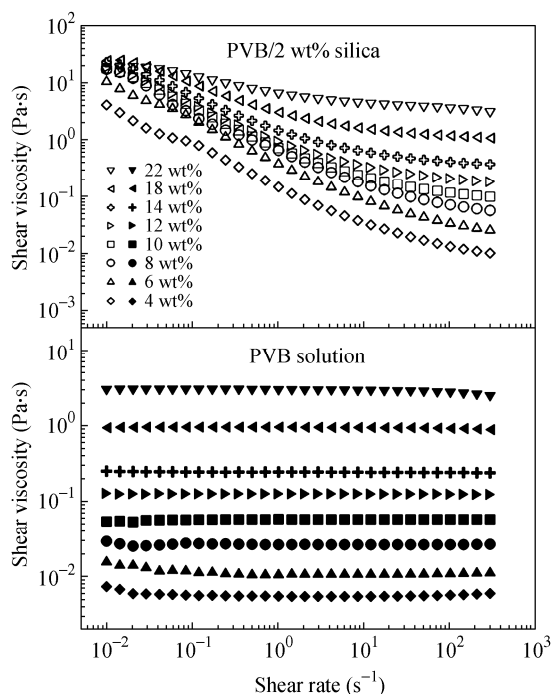


Fig. 2 Comparison of viscosity curves of neat PVB and PVB/silica solutions (Silica concentration is at 2 wt%).

Cassagnau^[17] explained the nonlinear behaviour of molten polymer including fumed silica through two mechanisms. In the first, particles of silica favour self-aggregation and creation of a three-dimensional network in the polymer matrix due to their fine size and high specific surface area. The second-order mechanism originates at sites of polymer-silica interaction.

In the following, oscillatory tests were carried out to determine the viscoelastic properties of the PVB and PVB/silica solutions. The neat PVB solution shows typical Newtonian behaviour, hence merely viscous modulus (not presented herein). The results displayed in Fig. 3 demonstrate the frequency dependencies of the two chosen PVB/silica solutions of the lowest and highest polymer concentrations.

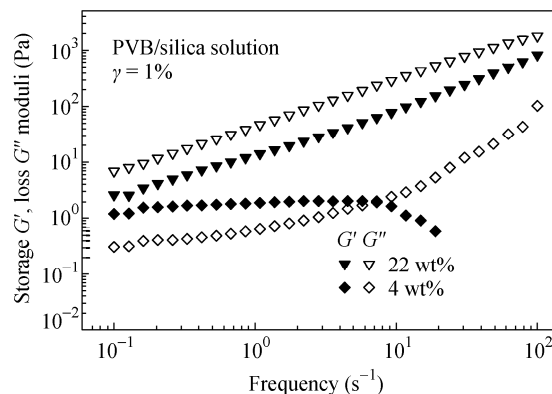


Fig. 3 Viscoelastic moduli of PVB/silica solutions (silica 2 wt%) within two limits of concentration

As can be seen, the frequency dependencies of the moduli are altered by the extent of polymer concentration. At low polymer concentration (4 wt%), the PVB/silica solutions exhibit higher elastic modulus than viscous modulus, by up to 10 s^{-1} . In contrast, viscous modulus dominates the entire frequency range utilized at higher polymer concentrations.

A clearer expression of viscoelastic properties is given through loss factor $\tan \delta$, relating to loss (viscous) G'' and storage (elastic) G' moduli ($\tan \delta = G''/G'$). It is apparent from Fig. 4 that silica has a favourable impact on the elasticity of the solutions, whereas neat PVB solutions demonstrate no elasticity ($\delta = 90^\circ$). The elasticity of the PVB/silica solutions is dependent on the concentration of the polymer. When polymer concentration is diminished (4 wt%–8 wt%), low phase angle values suggest a gel-like behavior, caused by the strong network structure of the interconnected silica particles. By increasing the concentration of the polymer (from 10 wt%), elasticity decreases correspondingly, which is due to prevailing polymer-polymer interaction, as manifested in the rise of the phase angle.

Extensive research by the authors demonstrates that a linear relationship exists between the rheology of a polymer solution and fibre diameter. Herein, it was found that a sufficiently high viscosity value favours smoother nanofiber formation, whereas electrospinning is not possible above the critical viscosity value. Figure 5 highlights that zero shear

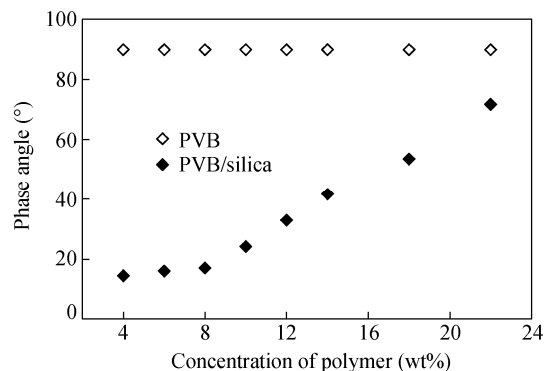


Fig. 4 The effect of concentration on the phase angle of neat PVB and PVB/silica solutions (silica 2 wt%) at frequency 0.5 s^{-1} and strain 1%

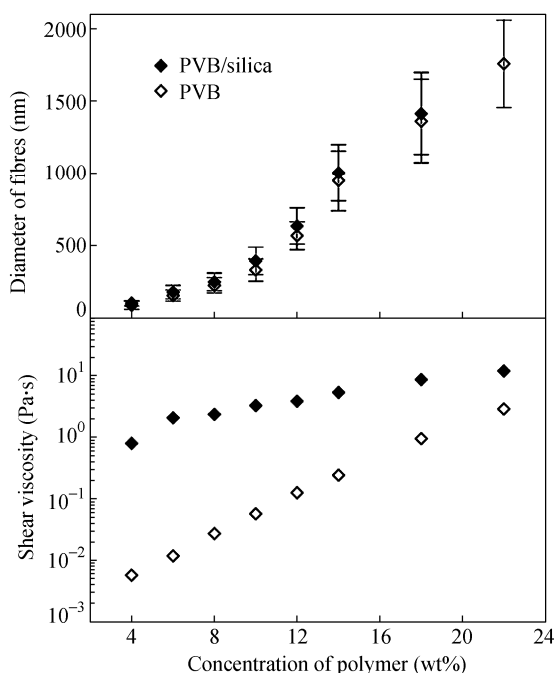


Fig. 5 Correlation between polymer concentration, viscosity of solution (at 0.1 s^{-1}) and the diameters of fibres

viscosity linearly increases alongside rise in concentration of the polymer solution. This trend is more pronounced in pure PVB solutions. Adding silica into the PVB solutions raises shear viscosity by two orders, although the diameters of the fibres remain very similar (Fig. 5). Thus, silica can assist in spinning less viscous polymer solutions. It proved impossible to spin the highest concentrated (22 wt%) PVB/silica solution, which corresponds to the zero shear viscosity value of $12.6 \text{ Pa}\cdot\text{s}$.

The quality of the electrospun fibres was evaluated by SEM analysis, which turned out to be dependent on the concentration of the polymer solution (Fig. 6). Nanofibre morphology predominantly takes the form of a circular cross section. Neat PVB fibres are uniform in diameter, while bead defects are not observed above the PVB concentration 8 wt%. However, the final cross section of microfibers created from the more highly concentrated solutions (exceeding 14 wt%)

was more complex. In comparison, the PVB/silica fibres possessed larger diameters and broader distributions in such size. The silica caused the surfaces of the fibres to be rough, while increasing the PVB content (from 14 wt% to 18 wt%) failed to result in any significant change to said surfaces.

The Effect of Silica Concentration on the Performance of Electrospinning

Study was made as to the effect exerted by the concentration of silica on the 10 wt% PVB solution, the concentration at which nanofibres are still produced. Additionally, the influence of silica concentration on the surface tension and conductivity of the PVB solution was investigated (see Fig. 7). Adding more silica nanoparticles into the fixed concentration of the PVB solution triggered merely an insignificant alteration in surface tension and conductivity.

The shear viscosity of the PVB/silica solution directly relates to rise in silica concentration. Figure 8 details viscosity measurements in terms of dependence on shear rate. Predictably, shear viscosity increases in parallel with greater silica concentration, while the shear-thinning behaviour of the solutions is also more pronounced.

Likewise, the elasticity of the PVB/silica solutions increased alongside parallel rise in the concentration of silica, up to the critical value of 2 wt% (see Fig. 9). It would seem that elasticity is constant once this concentration of silica is exceeded. The role of elasticity is often correlated with the

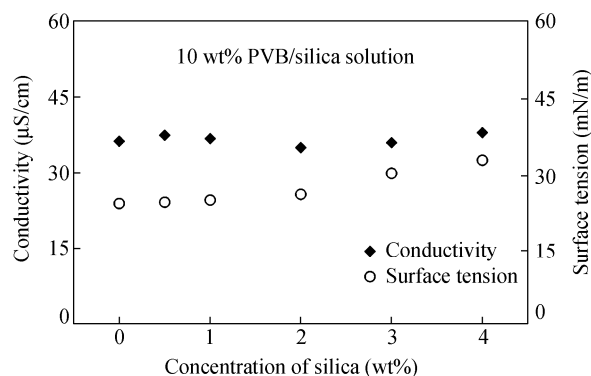


Fig. 7 The effect of silica concentration on the surface tension and conductivity of 10 wt% PVB solution

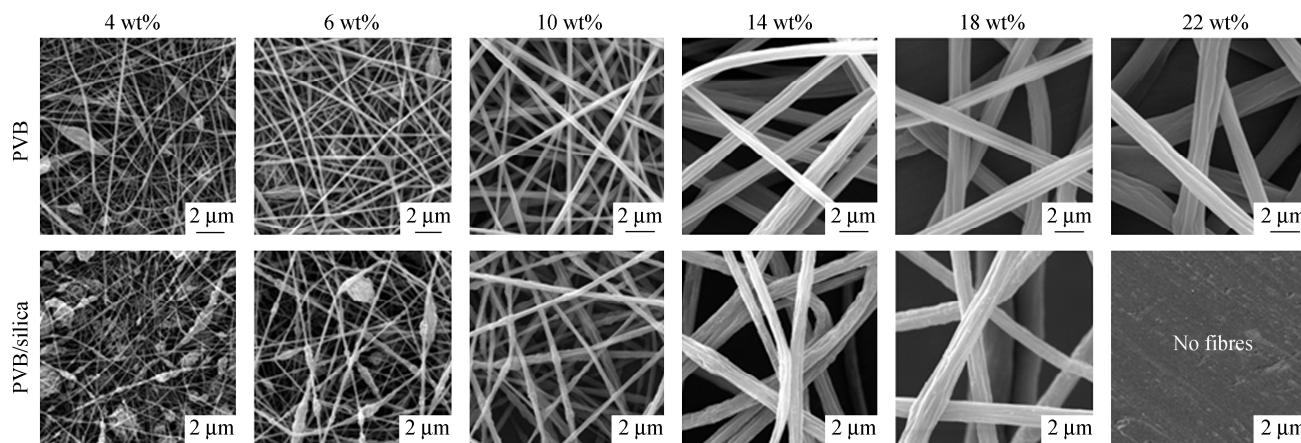


Fig. 6 The effect of concentration on the quality of neat PVB and PVB/silica fibrous webs (silica 2 wt%)

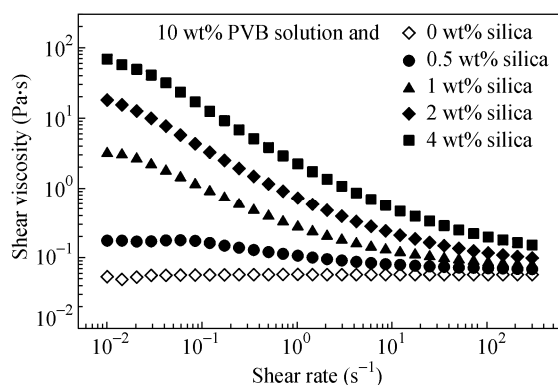


Fig. 8 The effect of silica concentration on the rheology of PVB solution (10 wt%)

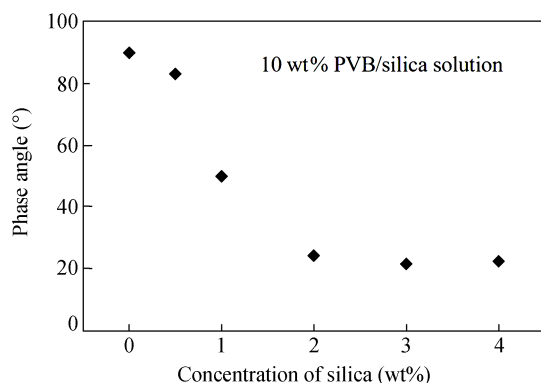


Fig. 9 The effect of silica concentration on the phase angle of PVB/silica solutions (PVB 10 wt%) at frequency 0.5 s^{-1} and strain 1%

diameter of the fibre, and it is a necessary condition for effectively carrying out the electrospinning process^[18–20]. Nevertheless, herein, raising the extent of elasticity had no significant effect on the diameters of the fibres, as previously discussed in the literature. Indeed, although the presence of silica significantly boosts elasticity, the solution becomes almost gel-like, yet it does not hinder initiation of the jet and the creation of fibres.

When producing fibres, adding silica NPs significantly influences fibre diameter and the roughness of the surface. Due to the increasing effect of viscosity, fibre diameter was enhanced (Fig. 10). At higher silica concentrations, the viscosity of the solution rose to $98 \text{ Pa}\cdot\text{s}$ at 0.01 s^{-1} . Nonetheless, electrospinning was immediately initiated and a fibrous web was created. In contrast, the 22 wt% PVB/silica solution (Fig. 5) demonstrated a viscosity limit for

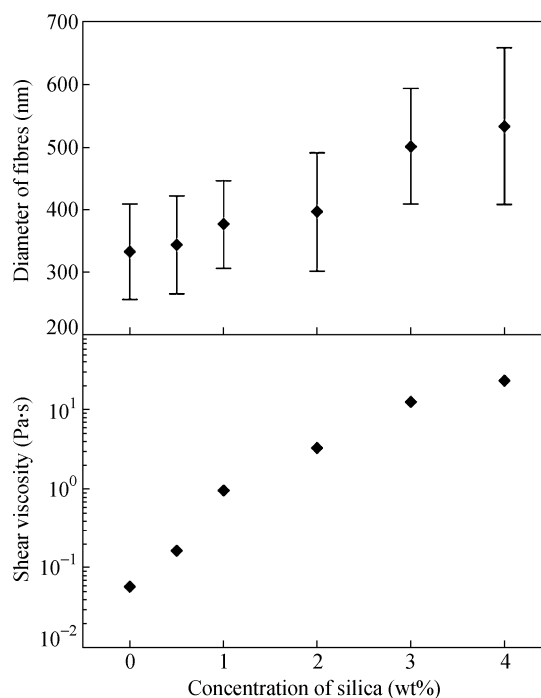


Fig. 10 The effect of silica concentration on the diameter of fibres and viscosity of the solution (at 0.1 s^{-1})

electrospinning of $15.9 \text{ Pa}\cdot\text{s}$ at the same shear rate. As clearly shown in Fig. 11, the roughness of the fibrous surfaces can be controlled by increasing the concentration of silica.

Characterization of Fibrous Webs

Comparison was made as to the thermal behaviour of neat PVB and PVB/silica fibres. Table 1 lists data on characteristic temperatures and total weight loss. The extrapolated onset temperature (T_{onset}), defined as the intercept of extrapolated starting mass with the tangent applied to the maximum slope of the TG curve, and T_{max} , corresponding to the temperature of the peak maximum on the DTG curve, were evaluated according to the reference given^[21].

Different decomposition behaviours were observed. The neat PVB fibres were almost fully decomposed at around 650°C . However, the amount of ash of the PVB/silica sample

Table 1 Characteristic parameters of TGA analysis pertaining to the neat PVB and PVB/silica samples

Sample	$T_{\text{onset}} (^\circ\text{C})$	$T_{\text{max}} (^\circ\text{C})$	Total weight loss (%)
Neat PVB	365.1	393.5	99.9
PVB/silica	380.2	401.1	83.6

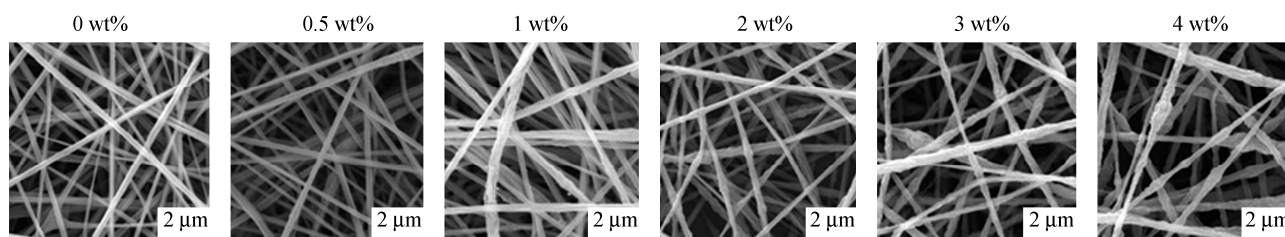


Fig. 11 The effect of silica concentration on the quality of PVB/silica fibrous webs (PVB 10 wt%)

after thermal decomposition equalled 16.4 wt%. This finding was attributed to silica nanoparticles that had been confirmed by FTIR analysis (see Fig. 12), which is also in good agreement with the amount of silica contained in the sample. Taking into account the characteristic temperatures determined, it seems that the silica nanoparticles had improved the thermal stability of the PVB fibres.

The chemical structures of both the neat PVB and PVB/silica fibrous samples were analysed by FTIR. A comparison of the infra-red ATR spectra is presented in Fig. 12. A broad band corresponding to the —OH group in the range 3200–3600 cm^{-1} is noticeable, together with the stretching modes of C—H in the range 2750–3000 cm^{-1} . Moreover, the bending modes of C—H groups are also discernible in the range 1300–1500 cm^{-1} . However, it was observed that important differences existed in the C—O—C group band in the range 950–1200 cm^{-1} . The bands determined at wavenumbers of 1132, 1107 and 1053 cm^{-1} are typical for PVB. These are clearly visible in the measured spectra in Fig. 12. But their shapes seem to be little affected in the case of PVB/silica sample (see spectrum in the middle part in Fig. 12). The band at 1053 cm^{-1} disappeared in this case. Taking the composition of prepared sample into account, the presence of silica is only one reason that can lead to the described changes. Moreover, the presence of silica in the sample labeled as PVB/silica was confirmed later. Consequently, the ash of the PVB/silica sample (following TGA analysis) was investigated again by FTIR. The characteristic bands corresponding to Si—O—Si vibrations were confirmed by comparing the spectrum measured herein with the available library.

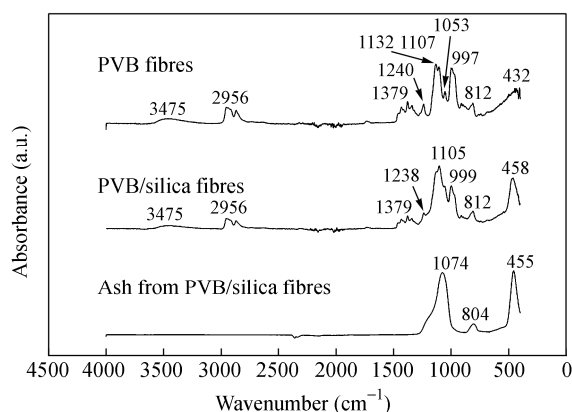


Fig. 12 FTIR spectra for PVB and PVB/silica fibres

CONCLUSIONS

Various fibrous PVB/silica webs were prepared by electrospinning solutions that contained hydrophobic fumed silica and PVB in methanol. In this work, it was found that the PVB/silica solutions possessed far greater shear viscosity and elasticity than the neat PVB solutions. It was demonstrated that a means for controlling rheological properties was to vary the concentration of PVB or silica. Nevertheless, the significant differences in the rheological parameters

discovered, as influenced by the content of silica, did not at all impact the ability to spin fibres. The authors concluded that the rheological properties pertaining to the PVB/methanol system containing the particles of silica were not as pivotal as reported previously in the literature. The thermogravimetric measurements carried out by the authors corroborate that the silica nanoparticles actually improved the thermal stability of the PVB fibres, which could prove useful in future applications.

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