Effect of Ceramic Nanoadditive Content and Type on the Rheological Properties of Poly(vinyl alcohol) Spinning Solutions

Maciej Boguń, Teresa Mikołajczyk

Department of Man-Made Fibres, Technical University of Lodz, Lodz 90-924, Poland

Received 10 August 2008; accepted 27 April 2009
DOI 10.1002/app.30728
Published online 12 August 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Rheological properties of aqueous PVA solutions within a wide concentration range have been examined to select a concentration at which apparent dynamic viscosity is suitable for fiber spinning from solution by the wet process. The rheological properties of PVA solutions containing various quantities of nanosilica and nanohydroxyapatite were assessed. It has been found that an increase in the quantity of both types of nanoadditives from 1 to 5% brings about a decrease in the value of the rheological parameter *n* and enhances the polymeric character of the fluid.

Key words: additives; biopolymers; nanocomposites; rheology

INTRODUCTION

One of the biodegradable, biocompatible, and nontoxic polymers that at present play a significant part in the biomedical engineering is poly(vinyl alcohol) (PVA).[1–3] Because of its chemical structure, it is characterized by highly hydrophilic properties and the capability to gelatinize. Nowadays, PVA is used in biomaterial engineering in the form of composites with other materials as well as in the form of hydrogels, among other things, to regenerate tendons and chondral parts,[4,5] in ophthalmology,[6] pharmacy,[7] and tissue engineering.[8,9]

A new application of this polymer in biomedical engineering could be the production of nanocomposite PVA fibers by the wet process from solution, owing to the fact that this process, as opposed to other conventional fiber spinning methods or modern electrospinning, makes it possible to appropriately control process parameters to obtain deliberate, reproducible fiber structures and properties. This process also allows one to produce fibers with various chemical compositions and molecular weights showing anisotropy of properties, as natural tissues whose properties are connected with the presence of fibrillar proteins. Such nanocomposite fibers will be designed for the production of porous composites containing other biocompatible and biodegradable polymers, e.g., PGLA, ε-caprolactone. The resulting biocomposites will be capable of releasing bioactive nanoparticles during polymer biodegradation. The incorporation of bioactive nanoadditives such as SiO_2 or hydroxyapatite into PVA fibers will make it possible to impart osteoconductive and osteoproductive properties to implant materials made from these fibers. The use of silica such as Hap in biomaterials engineering has already been described extensively in a number of works.[10-23] Their presence in fibers will cause new unique properties in composite materials made on the basis of a warp of nanocomposite PVA fibers.

The presence of nanoadditives in a spinning solution also affects its rheological properties, processability into fibers, and the performance properties of the produced fibers. One of the parameters that influence the character of the rate distribution during fluid flow in the spinneret capillary, the course of relaxation processes in the off-spinneret zone, and the value of the lateral velocity gradient (changing along the fiber formation path) is the dynamic viscosity of liquid. In the case of excessive viscosity, the use of improperly selected take-up force can cause a fragile fracture, whereas insufficient viscosity results in capillary decomposition. In the wet process of fiber spinning from solution, there is a risk of both of these phenomena. The characteristics of polymer and spinning solution (polymer intrinsic viscosity, concentration in the solution, and apparent dynamic viscosity) also influence the course of the fiber formation process and the appropriate selection

Correspondence to: M. Boguń (maciek.bogun@wp.pl).
Contract grant sponsor: Minister of Science and Higher Education in 2007–2009; contract grant number: N50804932.

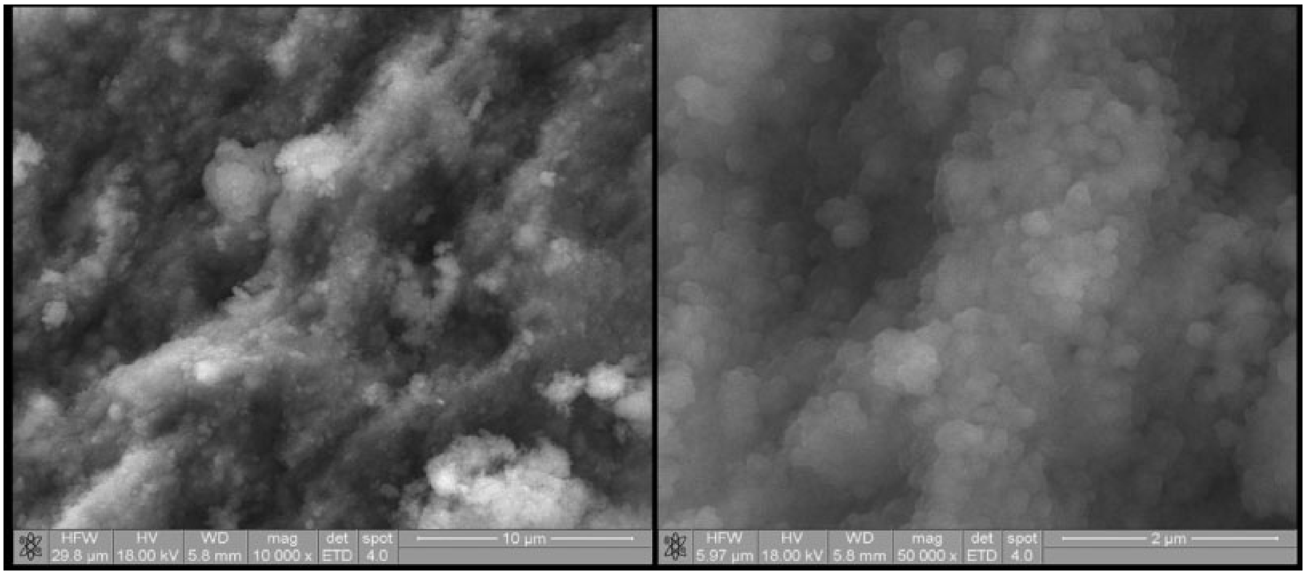

Figure 1 Photo of nanohydroxyapatite.

of process parameters affecting the fiber structure and properties. The rheological properties of spinning solution may also depend on the quantity and type of nanoadditive as well as its interactions with the solvent and polymer.[24,25]

We have found that the introduction of ceramic nanoadditives to a PAN spinning solution in DMF [26] and PIA in NMP [27] causes, as a rule, a decrease in rheological parameter n and an increase in rheological parameter k. The character of the fluid does not change. It is described by Ostwald de Waele's rheological model:

$$\tau = k \cdot Y_x{}^n$$

gdzie: n,k is the rheological parameters of the model, Y_x is the shearing rate, and τ is the sheaing stress.

For $n = 1$, the above relation describes the flow curve of a Newtonian fluid. For $n < 1$, the equation describes the flow curve of a liquid diluted by shearing, whereas for $n > 1$ it describes the flow curve of a liquid thickened by shearing. When the rheological properties of polymer liquids (alloys or solutions) are considered, the value n is taken to be a measure of the non-Newtonian behavior of the investigated liquid. [28]

The objective of this study is to assess the effect of the quantity and type of incorporated nanoadditives on the rheological properties of PVA spinning solutions in water as well as to select the proper content of nanoadditive in spinning solutions designed for the formation of nanocomposite PVA fibers to be used in biomaterial engineering.

The results of studies concerning the spinning conditions and properties of this type of fibers will be the subject of further publications.

MATERIALS AND METHODS

Poly(vinyl alcohol) JP 18 (Japan VAM & POVAL) was used in the study. Its intrinsic viscosity $[\eta] = 0.8$ dL/g was determined by the viscosimetric method in water at a temperature of 20°C. In this article, different mass concentrations of polymer in water were used. However, the percentage of nanoadditives was expressed in relation to the mass of polymer. The following nanoadditives were added to spinning solutions:

- hydroxyapatite (product of AGH Kraków) (Fig. 1),
- silica (product of Sigma-Aldrich) (Fig. 2).

The nanoadditives were added to spinning solutions in the form of suspension in water after being previously subject to ultrasonic treatment for 30 min by means of an ultrasonic sounder SonoPuls (Bandelin, Germany) with a power output of 50 W.

The characteristics of the nanoadditives are given in Table I.

The rheological properties of spinning solutions were determined using an Anton Paar (UK) rotational rheometer. The measurement was conducted with regard to the shearing speed of 145 L/s at the temperature of 20°C. Rheological parameters n and k were determined on the basis of flow curves.

RESULTS AND DISCUSSION

The basic issue in fiber spinning by the wet process from solution is to find the right spinning solution concentration. It should be at such a level that the apparent dynamic viscosity would enable spinning

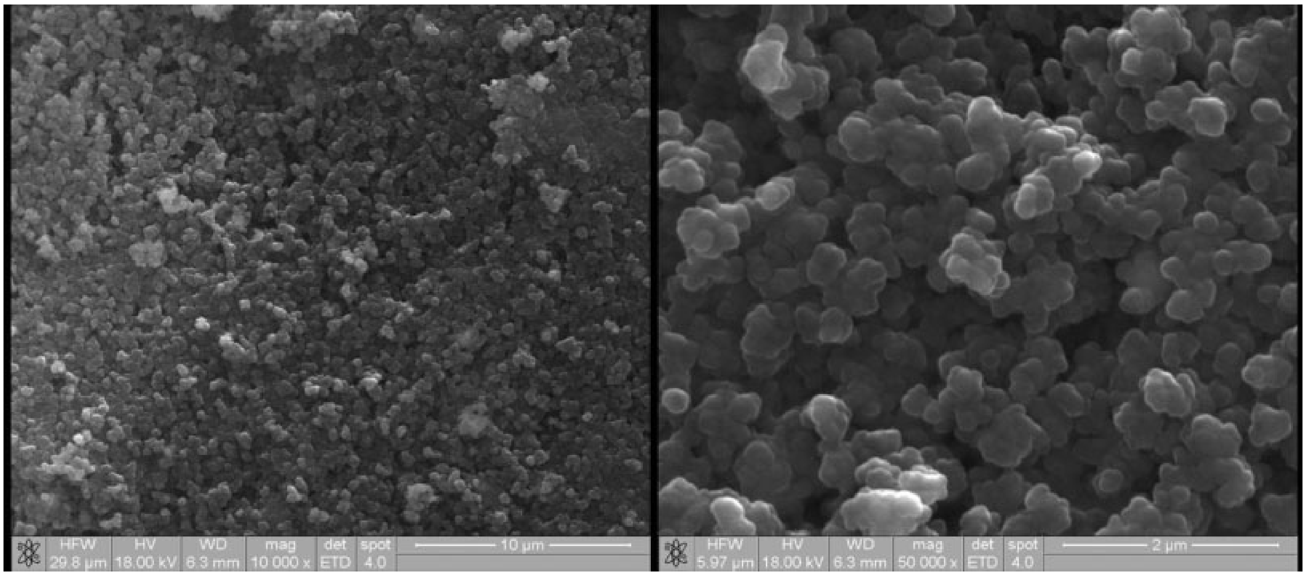

Figure 2 Photo of nanosilica.

possible on a typical spinning machine without breaking elementary filaments at the spinneret. The used concentrations ranged from 18.5 to 21%. The polymer content in the solution cannot be too high as, according to our previous studies, [29] the presence of nanoadditives in the solution was in some cases accompanied by an increase in its apparent dynamic viscosity.

From the flow curves shown in Figure 3, it follows that the highest position is occupied by the flow curve of the solution with a polymer content of 21%. In all cases, tangential stress increases less than proportionally with an increase in the shearing rate, while the curves pass through the origin of coordinates. This shows that the solutions are non-Newtonian liquids rarefied by shearing without a flow limit. The decrease in the spinning solution concentration makes it more like a Newtonian liquid. At the same time, its character becomes less polymeric, while the curves illustrating the dependence of apparent dynamic viscosity on the shearing rate show a flatter shape (Fig. 4). This is accompanied by the lowest value of rheological parameter *k* being a measure of solution consistency. Such rheological properties of PVA spinning solutions in water are consistent with the generally known facts.[28]

Based on the analysis of apparent dynamic viscosity values, a solution containing 20% of PVA was selected for further tests. From our studies into nanocomposite fiber spinning from various fiber-forming polymers, it follows that solutions with similar characteristics show good processability into fibers. The use of a higher concentration, e.g., 20.5%, causes that the dynamic viscosity of solutions of about 39 mPa s may be too high when nanoadditives are added to them.

Based on the analysis of the obtained flow curves (Figs. 5 and 6) of 20%, PVA JP 18 spinning solutions containing 1, 3, and 5% of silica (in relation to polymer), one can state that these solutions are non-Newtonian liquids rarefied by shearing without any flow limit. A similar character of flow curves is observed in the case of spinning solutions of polymer containing nanohydroxyapatite. In all the cases, tangential stress increases less than proportionally with an increase in the shearing rate, while the curves pass

TABLE I
Characteristic of Nanoadditives

Type of nanoadditive	Particle size (nm)	Specific surface (m^2/g)
SiO_2	10–150	563.5
Hydroxyapatite	30–500	73.6

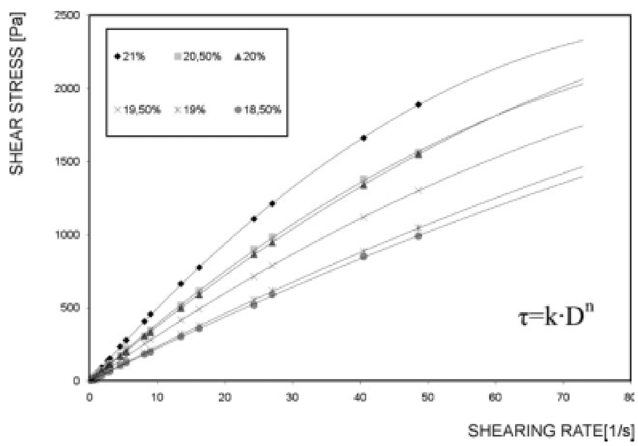

Figure 3 Dependence of shearing stress on the shearing rate for different concentration PVA solutions in water.

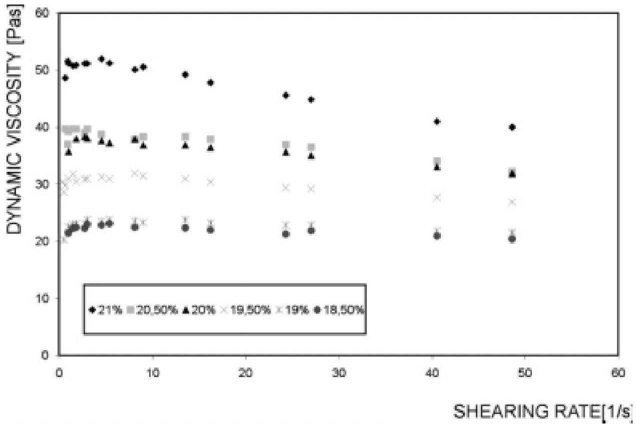

Figure 4 Dependence of dynamic viscosity on the shearing rate for different concentration PVA solutions in water.

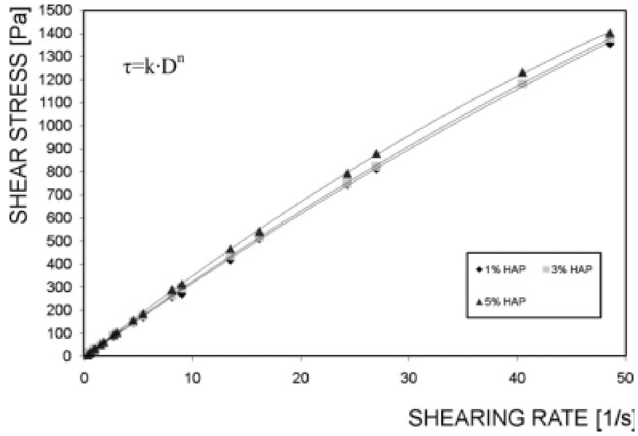

Figure 6 Dependence of shearing stress on the shearing rate for 20% PVA solutions in water containing nanohydroxyapatite.

through the origin of coordinates. On the other hand, apparent dynamic viscosity decreases with an increase in the shearing rate, which is typical of polymeric liquids, and an increase in the nanoadditive content does not change the character of this relationship (Figs. 7 and 8). The investigated solutions show stability of the rheological parameters n and k over a time of 72 h. The flow curves obtained are practically identical to the curves in Figures 3, 5, and 6, and for this reason they are not shown in this article. The time of 72 h is sufficient for deaeration and filtration of the spinning solution and for the carrying out of the forming process.

The addition of low quantities of nanoadditives (hydroxyapatite as well as silica) brings about only an insignificant change in the rheological parameter n. Its value for both nanoadditives is at a similar level: 0.984–0.987 (Table II).

The value of rheological parameter k, being a measure of solution consistence, is also at a similar level. This value of a solution containing 1% of SiO_2 or HAp is lower than that of a solution containing no nanoadditive, which indicates that such a low content of nanoadditive influences the rheological properties of spinning solutions only to a small extent. On the other hand, an increase in the content of each of the nanoadditives of up to 5% brings about a considerable change in the parameter n and intensifies the non-Newtonian character of the spinning solution (Figs. 5 and 6) when compared with that of a PVA solution with no nanoadditive.

In the case of both nanoadditives, it has been found that increasing nanoadditive content makes the non-Newtonian character of liquid more and more visible, as confirmed by the decreased value of parameter n and a simultaneously increased parameter k (Table II). However, the parameter k in solutions containing SiO_2 was slightly higher and if the content of SiO_2 was 3 or 5%, it is similar to that of the solution with no nanoadditive. This may be due to the highly specific surface of SiO_2 causing its strong interaction with the solvent, which results in a more polymeric character of the liquid. There is a similar effect to the influence of polymer molecular

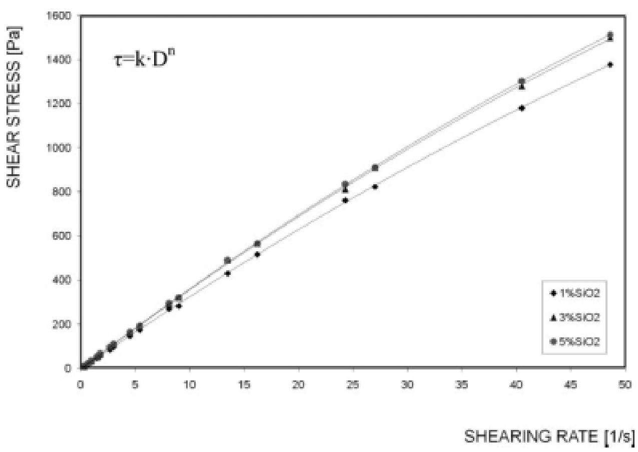

Figure 5 Dependence of shearing stress on the shearing rate for 20% PVA solutions in water containing nanosilica.

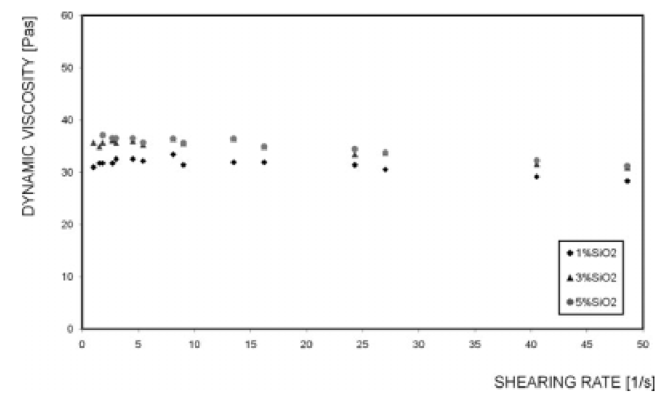

Figure 7 Dependence of dynamic viscosity on the shearing rate for 20% PVA solutions in water containing nanosilica.

weight and concentration on the value of parameter *k*. In comparison with this, solutions containing HAp with a considerably smaller specific surface show lower values of parameter *k* than that of solutions containing no nanoadditive.

The addition of both types of nanoadditives in the quantities of 1–5% to spinning solutions intensifies the non-Newtonian character of the liquid and increases the effect of rarefaction by shearing. In accordance with the accepted explanation of rarefaction by shearing,[28] immovable liquid contains considerably kinked PVA macromolecules. Their effective dimensions with the immobilized continuous phase (solvent) are considerable, especially because of the possibility of hydrogen bonds formation between PVA macromolecules and the solvent (water). This effect is intensified by the susceptibility of water to form polymorphous clusters.[30] It can be also intensified by the presence of SiO_2 or nanohydroxyapatite inside the kinked macromolecules and between them. An additional intensifying factor is also the susceptibility of nanoparticles to agglomerate and interactions between the nanoadditive and solvent. During shearing, polymer chains are gradually straightened and dekinked as the shearing rate rises. This results in a progressive decrease in the internal friction of the system because of the smaller dimensions of macromolecules and weaker interactions between them. These interactions become weaker also because of the presence of SiO_2 or HAp between macromolecules. The presence of nanoadditives in the system also influences the course of phenomena connected with solvation, explaining the mechanism of rarefaction by shearing. This concerns both the addition of molecules in the continuous phase (solvent) to polymer macromolecules and the interactions of SiO_2 and Hap with the solvent. The gradual tearing off of the solvation sheath with an increasing shearing rate brings about a decrease in the internal friction of the system. In the case of SiO_2 with a large specific surface and strong interactions with

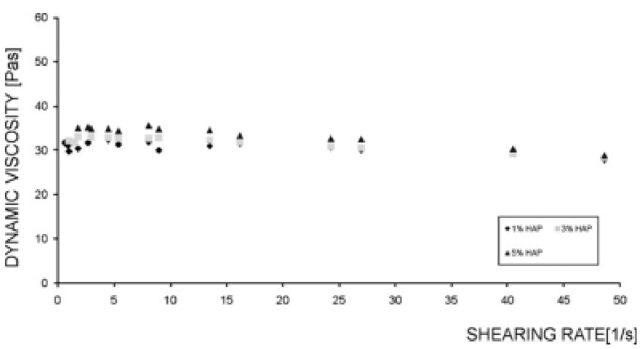

Figure 8 Dependence of dynamic viscosity on the shearing rate for 20% PVA solutions in water containing nanohydroxyapatite.

TABLE II
Rheological Properties of 20% PVA Spinning Solutions in Water Containing Various Contents of Ceramic Nanoparticles

Solution symbol	Nanoadditive	Nanoadditive content (%)	Rheological parameter	
			n	*k*
J 0	None	0	0.992	36.28
JH 1	HAp	1	0.984	31.92
JH 2	HAp	3	0.983	32.65
JH 3	HAp	5	0.971	35.59
JS 1	SiO_2	1	0.987	32.13
JS 2	SiO_2	3	0.977	36.32
JS 3	SiO_2	5	0.974	36.92

the solvent, the effect of its presence on the tearing off of the solvation sheath is smaller than that of HAp. Because of the small specific surface of Hap, its interactions are weaker, which facilitates the tearing off of the solvation sheath. The internal friction of the system: macromolecule-solvent-nanoadditive decreases with an increase in the shearing rate to an extent being also dependent on interactions between the nanoadditive and solvent. The effects of it are the discussed differences in the values of rheological parameters *n* and *k* of both nanoadditives.

A similar character of changes in the parameters *n* and *k* was found by us in the case of solutions of other fiber-forming polymers containing ceramic,[26] ferromagnetic [29] nanoadditives.

CONCLUSIONS

1. Considering the processability of a PVA spinning solution, it is useful to maintain its concentration at a level of 20%, which ensures a dynamic viscosity of about 35.71 mPa s, a value typical of fiber spinning by the wet process from solution.
2. The addition of nanoadditives such as SiO_2 and HAp to a spinning solution does not change the rheological character of the liquid, but affects the values of rheological parameters *n* and *k*. These values depend not only on interactions between polymer macromolecules and solvent molecules but also on surface interactions with the added nanoadditive.
3. An increase in the nanoadditive content from 1 to 5% brings about a decrease in the rheological parameter *n* and enhances the polymeric character of the liquid.

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