

Alkoxide-Based Precursors for Direct Drawing of Metal Oxide Micro- and Nanofibres.

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ABSTRACT

In this study, the comparative analysis of different parameters of spinnable metal alkoxy precursors for metal oxide fibre drawing is presented. The precursor samples were obtained from tin 1-butoxide $\text{Sn}(\text{OBU})_4$ as a result of aqueous (AQ) and non-aqueous (NAQ) (thermolysis) treatment. Rheological tests have proved that the solvent free precursors are typical non-Newtonian fluids. Precursors obtained with the help of NAQ treatment are more elastic as compared to those prepared with AQ procedure. Surface tension (ST) measurements show that the coefficient of ST of NAQ prepared precursor is 45% lower than that of AQ prepared one. Fibres with aspect ratio up to 10000 and diameter of 200 nm were directly drawn from the NAQ precursors at room temperature in standard lab atmosphere. AQ prepared precursor allows obtaining of the fibers of minimum 500 nm in diameter with maximal aspect ratio 1000.

Keywords: tin alkoxide, sol-gel, rheology, metal oxide nanofibre

1 INTRODUCTION

Nowadays there is a well-recognized need in materials for high-tech applications such as temperature resistant layers, high refractive index materials, photonic materials, transparent electrodes, abrasives, constructing materials etc. Metal oxide ceramics may be used successfully in these applications. However, one of the limitations in wide application of these materials is difficulties in their preparation in a required shape.

The sol-gel process is of special interest because it enables to obtain different geometries by gelling the structures in suitable molds, as thin films, jets pulled into air etc [1]. The method also has many other advantages such as much lower processing temperatures as compared to powder sintering, easy doping with different additives, relative cheapness and easiness to scale up the processes. As final shape is not a task achievable just by chemical

processes then different mechanical manipulations are used to do it like dip- and spin-coating to prepare thin films, molding to achieve specific microscopic geometries or drawing (spinning) to get the fibres [2, 3].

In this study, aqueous (AQ) and non-aqueous (NAQ) [4] precursor treatments were applied to prepare precursors from $\text{Sn}(\text{OBU})_4$. Two different chemical approaches under kinetically unhindered nucleation conditions still lead for rather similar product: metal oxo alkoxides – small (partially) crystalline oxide nanoparticles, some nanometers in size, stabilized by shell of alkoxy groups [5]. The precursors allow obtaining of the fibers of different minimal diameters despite of the identical conditions of drawing. Sizes of the fibers depend on rheological characteristics of liquids and surface tension that is determined by inner structure of the liquid. The aim of this study is a comparative investigation of the rheological characteristics of the spinnable precursors, which were obtained from $\text{Sn}(\text{OBU})_4$ as a result of aqueous (AQ) and non-aqueous (NAQ) treatment.

2 PRECURSOR PREPARATION

2.1 AQ Condensation of $\text{Sn}(\text{OBU})_4$

Synthesis of $\text{Sn}(\text{OBU})_4$ is described elsewhere [6]. After removal of solvents in vacuum, the alkoxide was obtained as viscous syrup-like brown liquid.

Initially, 5 g alkoxide aliquots were used for precursor preparation. To initiate the condensation, water was added for the samples as 5 % solution of butanol, acidified with ~20 mg of concentrated (~35%) HCl water solution. To transform the obtained mixtures into viscous fibre drawing dopes, solvents and low molecular mass organics in materials were evacuated at 1-2 torr vacuum and 70 °C water bath. A detailed rheological analysis was performed for $\text{Sn}(\text{OBU})_4$ based samples obtained for water/alkoxide mole ratio $R = 0.7$ that exhibited the optimal properties for fibres drawing.

2.2 NAQ (Thermolysis) Condensation of Sn(OBu)₄

Thermal condensation of Sn(OBu)₄ has been carried out in a rounded reaction bulb at slow temperature increase during 8 hours. The final temperature of thermolysis experiments was set 275 °C as a temperature when the system transformed into oxide. To make heat distribution uniform, a silicone oil bath was used. In order to remove volatile organics, the thermolysis was maintained at a low vacuum of about 1-5 torr. Evacuated gases were trapped in a condenser that was cooled down to the temperature of liquid nitrogen. After each removal of around 5-10% of substance mass, the bulb was back flushed with dry argon and the reaction was stopped for approximately 3 minutes for taking the precursor samples out. As a result of the experiment, 2-3 g aliquots of 7 potential precursors (fractions 1-7) were prepared and sealed into plastic syringes for further analysis and fiber drawing tests. For rheological analysis, fraction 5 with the optimal spinnability was used. For this particular fraction Sn(OBu)₄ was heat-treated up to 170 °C under vacuum of 1 torr.

3 STRUCTURE OF PRECURSORS

SAXS determined pair distribution functions (Fig. 1) and DAMMIN 3D [7] modeling of observed scattering patterns of Sn(OBu)₄ based samples showed elongated particle shape. The particles of both AQ and NAQ prepared precursors were found to be of 3 – 5 nm in length and 2 nm in diameter. Metal oxo-alkoxides are known to exist as small ball-shaped nanoparticles [5], hence their elongated shape could be explained by formation of secondary particles. Such behavior of metal alkoxides is well-known [5] and could finally lead to gelation of system as a result of 3D solid network development. The size of a pure Sn(OBu)₄ may represent a mixture of tri- and tetramers and show dimensions of 0,9 nm in diameter and 2 nm in length.

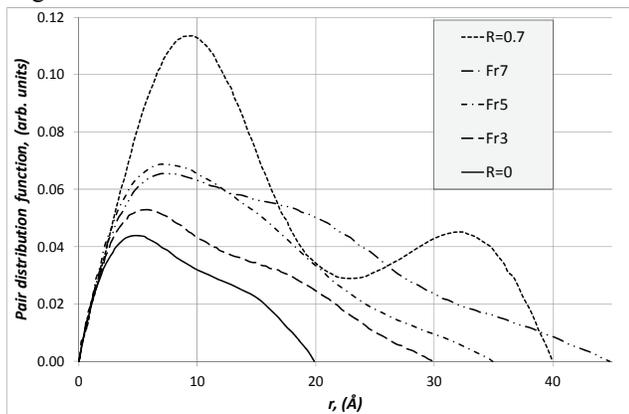


Figure 1: SAXS pair distribution functions P(r) of AQ and NAQ prepared Sn(OBu)₄ precursors.

4 RHEOLOGICAL STUDIES

Influence of shear rate on viscosity is shown in Figure 2. It may be suggested that the synthesized initial Sn(OBu)₄, AQ and NAQ treated Sn(OBu)₄ exhibit a typical behavior of a non-Newtonian liquids. All liquids reveal a decrease in the apparent dynamic viscosity with an increase in shearing rate, which is typical for polymeric liquids and could be argued in a current case by sliding of linear-shape particles that orient and start sliding if stress is applied. Initial Sn(OBu)₄ has pronounced zero shear plateau and shear thinning may be described by Cross model

$$\eta = \frac{\eta_0 + \eta_\infty \cdot (K \cdot \dot{\gamma})^m}{(K \cdot \dot{\gamma})^m + 1} \quad (1)$$

Dependences of viscosity on shear rate for precursors are described by Sisko model, which is relevant for structured liquids

$$\eta = \eta_\infty + \frac{\eta_0}{(K \cdot \dot{\gamma})^m} \quad (2)$$

K and *m* parameters of the models are given in Table 1 for the liquids studied.

Sample	<i>K</i> (s)	<i>m</i>
Sn(OBu) ₄	1.1	1.5
AQ prepared	19.33	1.37
NAQ prepared	9.82	1.30

Table 1: The values of model parameters of Sn(OBu)₄ systems.

Constant viscosity values of 0.58, 121, 273 Pa·s for initial Sn(OBu)₄, AQ and NAQ prepared Sn(OBu)₄ were obtained when the shear rates of 100 s⁻¹ was applied. The viscosity of NAQ is two times higher than AQ at high frequencies. At the same time shear thinning behavior (value of *m*) of AQ is more pronounced.

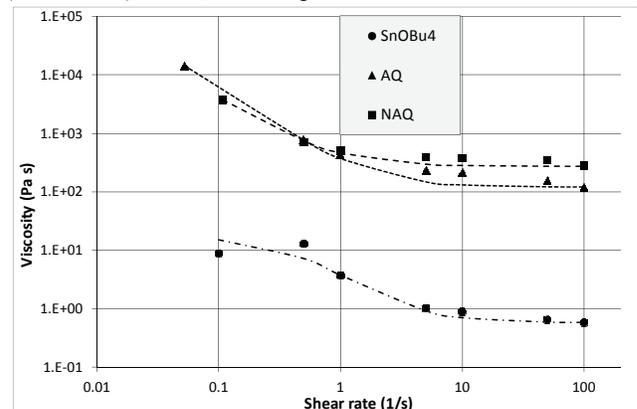


Figure 2: The viscosity values of Sn(OBu)₄ systems.

To obtain comprehensive and reliable information on the rheological state of the alkoxide systems, oscillatory measurements of viscous and elastic properties were performed. Firstly, values of storage G' (elastic response) modulus were measured to determine the linear viscoelastic region where the structure of the dispersion keeps intact. Measurements were made at frequency of 10 rad/s. Figure 3 shows that NAQ treated $\text{Sn}(\text{OBU})_4$ has the widest linear viscoelastic region. Just at the strain amplitude higher than 2% the system reveals the breakdown of the network. Initial $\text{Sn}(\text{OBU})_4$ and AQ treated $\text{Sn}(\text{OBU})_4$ have roughly the same linear viscoelastic region of the stable network up to 0.2% strain amplitude.

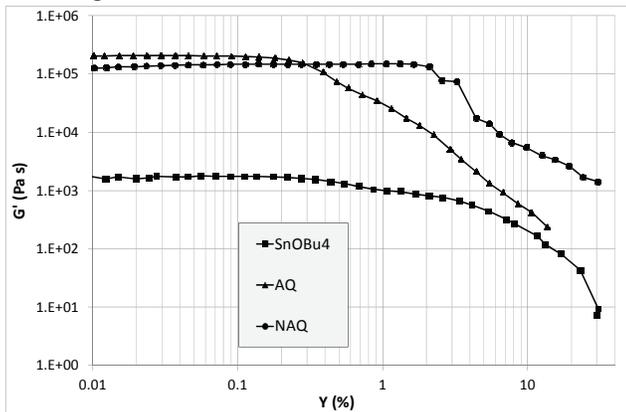


Figure 3: Determination of linear viscoelastic limit for $\text{Sn}(\text{OBU})_4$ systems.

The frequency sweep results for the tin alkoxide systems at strain amplitude 0.1% (within the linear viscoelastic region) are presented in Figure 4. All the samples show excess of storage G' (elastic response) modulus over loss G'' (viscous response) modulus and the power law dependence of modulus in the examined diapason of frequency. Consequently a predominantly elastic behavior is indicated for both systems. Power exponent of storage G' modulus for AQ and NAQ are 0.14 and 0.03, respectively, while exponent of loss G'' modulus are relatively similar and equal to 0.15. Low value of exponent of storage G' modulus is related to a high elastic system [8] indicating that intermolecular cross-links of NAQ prepared precursor are stronger.

The crossover point between G' and η^* points to the fact that particle weight of NAQ precursor is somewhat larger as compared to AQ precursor at the identical value of particle weight distribution.

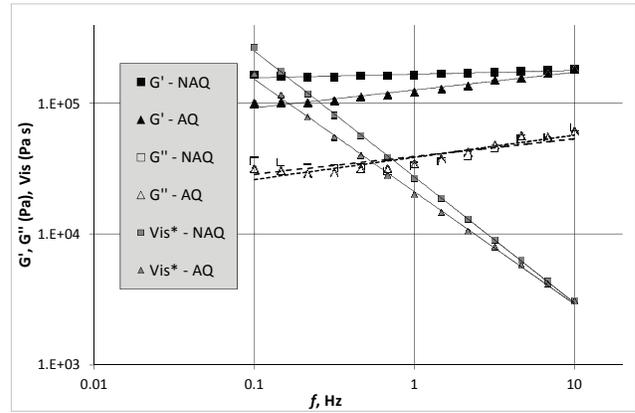


Figure 4: Viscoelastic properties (η^* ; G' ; G'') of tin alkoxide systems.

As process of fibre formation is influenced by surface tension (ST), the measurements of ST coefficients were performed for the liquids of interest. Because of high reactivity of the liquids against humidity, the tests were made in the bulbs by inverted vertical pull surface tension method as described in [9]. The initial $\text{Sn}(\text{OBU})_4$, AQ and NAQ prepared $\text{Sn}(\text{OBU})_4$ exhibited the coefficient of ST of 26.6, 32.7 and 18 mN/m, respectively. Nearly twice higher of ST in AQ treated samples could be explained by stronger intermolecular forces in AQ prepared precursors. We suggest that the strength of the forces between the precursor particles is defined mostly by density of oxide cores. Sn-centers laying directly on the surface of denser NAQ particles are less acetic in Lewis sense and show up less tendency to form intermolecular bonds.

5 METAL OXIDE MICRO- AND NANOFIBRES

Fibres of aspect ratio up to 10000 and diameter 200 nm were directly drawn from the precursors by different manipulations carried out at room temperature in standard lab atmosphere. The fibers, drawn from AQ treated precursor samples, have a minimum diameter of 500 nm, while fibers drawn from NAQ fractions 4 and 5 have 200 nm in diameter. Aspect ratio of fibres pulled from AQ precursor remains 1000, contrary to 10000 in the case of NAQ precursor. The fibers produced in this study possess an ultra (Fig.5) high homogeneity and low surface roughness, which guaranty their excellent wave guiding properties with loss of 0.8 dB/mm or less.

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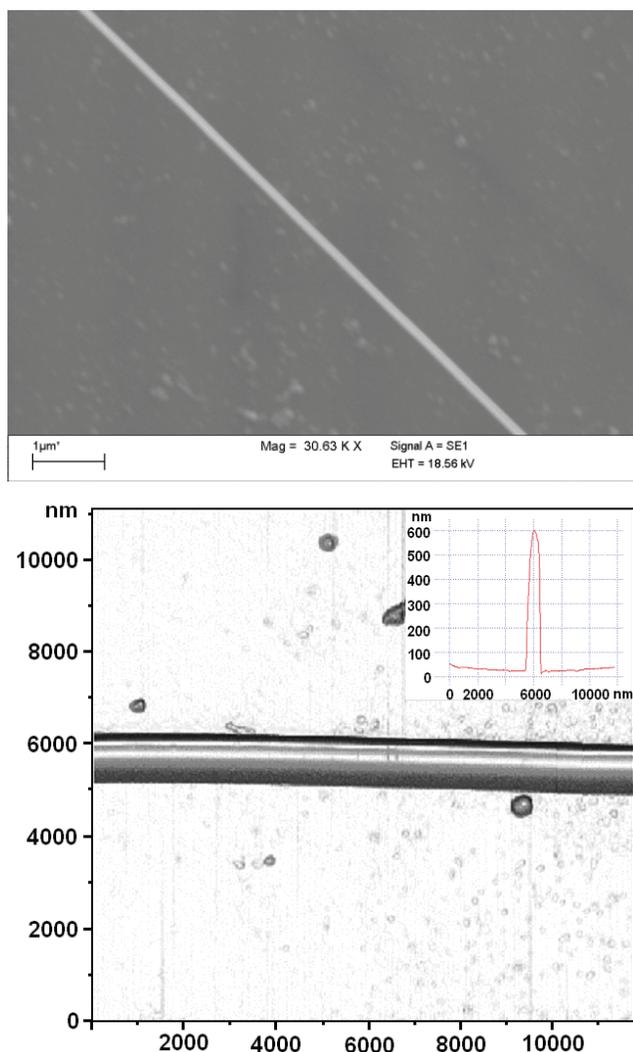


Figure 5: Images of SnO_2 fibres obtained from NAQ prepared $\text{Sn}(\text{OBU})_4$ precursors.

6 CONCLUSIONS

It was shown that $\text{Sn}(\text{OBU})_4$ precursors studied in this work consist of the elongated particles of 3 – 5 nm in length and 2 nm in diameter for both AQ and NAQ prepared precursors.

Rheological tests proved that metal alkoxide oligomeric precursors are typical non-Newtonian fluids. NAQ is revealing more elastic behavior as compared to AQ prepared $\text{Sn}(\text{OBU})_4$. Surface tension (ST) measurements show that the coefficient of ST of NAQ prepared precursor 45% lower than ST of AQ prepared one.

Under identical conditions, fibres directly drawn from NAQ prepared precursor have nano-scaled diameters of about 200 nm while fibres drawn from AQ prepared precursor have much larger diameters. Yet the aspect ratio of fibres pulled from AQ precursor remains 1000 while aspect ratio of fibres in the case of using NAQ precursor is equal to 10000.