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RHEOLOGICAL BEHAVIOUR OF TITANIA SYSTEMS DURING THE SOL-GEL TRANSITION

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ABSTRACT. Rheological behaviour of titania based systems prepared from the hydrolysis of titanium isopropoxide in ethanol-water mixture with different initial ratios between reagents has been studied. Rheological measurements in this study have established the dependence of gelation time upon the initial composition of raw materials. The achieved results have shown Newtonian behaviour of titania sols before gelation and non-Newtonian (pseudoplastic) behaviour after gelation.

Keywords: rheological behaviour, sol-gel transition, time of gelation, apparent viscosity, Newtonian and non-Newtonian fluids.

INTRODUCTION

Applications of the new low-temperature method for the synthesis of glasses, ceramics, mono-size powders, porous gels, membranes, coatings and thin films known as sol-gel have increased the interest in studying this possible route of preparation [1].

The sol-gel process is based on the hydrolysis of suitable molecular precursors and condensation of oligomers, thus the control of relative reaction rates allow to obtain materials that are more homogeneous than those obtained through conventional high temperature processes. The precursor participates in hydrolysis and condensation reactions forms particles (particulate sol) or polymers (polymeric sol), uniformly distributed in the bulk solvent [1, 2]. The particle-particle and particle-solvent interactions among these units lead to an increase in the viscosity of the solution until a *gel* is formed [3]. The sol-gel evolution has great influence in the porous structure of the final material, usually obtained after the application of a thermal program.

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The simplest picture of gelation is that clusters grow by condensation of polymers or aggregations of particles until the clusters collide; then links form between the clusters to produce a giant cluster that is called *gel*. At the moment that the gel forms, many clusters will be present in the sol phase, entangled in but not attached to the spanning cluster. With time, they progressively become connected to the network and the gel will increase. In this process no latent heat is evolved, but the viscosity rises abruptly and elastic response to stress appears [1].

Titanium dioxide (TiO_2) coatings (films) have been studied recently because of a large area of applications: solar cells, photo catalysis, photoelectric properties, antireflective coatings, electronic devices (dielectric mirrors for lasers), ceramic filters, as antibacterial coatings, self-cleaning coatings on car windshields, and protective coatings of marble (for preservation of ancient Greek statues against environmental damage) [4].

Sol-gel method is a relatively wide-spread method of producing TiO_2 coatings. The advantage of this method is the possibility to vary the film properties and low process cost. The sol-gel procedure may have the advantage of obtaining TiO_2 coatings with a smooth or a porous structure, depending on their uses. Controlled synthesis is essential for successful applications, and solution phase methods provide a large degree of control over the synthesis products [5].

The changes in rheological behaviour of materials are usually used to identify the *time of gelation*, t_g, and to establish the type of analysed systems (Newtonian or non-Newtonian fluid) [6, 7].

In this work, the sol-gel evolution of titania based systems using different initial compositions of raw materials has been analysed with a Rheotest 2 (type RV2, produced by Prüfgerate-Werk Medigan, Germany).

From the experimental obtained data, apparent viscosity (η_{app}) was estimated as:

$$\eta_{app} = \frac{\tau}{\gamma} \cdot 100 \text{ (mPa.s)} \tag{1}$$

where: τ is the shear stress (dyn/cm^2), and γ – shear rate (s^{-1}).

$$\tau = z \cdot \alpha \tag{2}$$

z is the constant depending on the type of used cylinder (z = 5.79 dyn/cm^2 for S-S$_1$ cylinders), and α is the electrical measurement read on Rheotest apparatus.

The analysis of the rheological behaviour of sol-gels TiO_2 performed in this study involves two types of correlations, the first one the modification of apparent viscosity (η_{app}) during sol-gel transition to identify the time of gelation for different initial ratios of the reagents, and the second one the variation of apparent viscosity (η_{app}) with the shear rate (γ) at constant time to establish the type of analysed systems (Newtonian or non-Newtonian material).

To confirme the behaviour of the TiO_2 gels as non-Newtonian material the model of power law (Ostwald de Waele) was used.

EXPERIMENTAL

a. PREPARATION OF MATERIALS

In this work, the synthesis of TiO_2 sol-gels was based on the hydrolysis of titanium isopropoxide ($Ti(O\text{-}iPr)_4$ or IPT). For the synthesis of the TiO_2 sol-gels were used: Ti(V) isopropoxide (>98%, Merck Schuchardt or 97 % Aldrich), anhydrous ethanol (analytical grade, Aldrich), deionised H_2O and HNO_3 (analytical grade, 65%, Primexchim).

The polymerization of formed oligomer in ethanol-water mixture was controlled kinetically with an inhibiting acid (HNO_3) that avoids the precipitation of the oxide or the formation of large heterogeneous zones. In order to obtain a homogenous mixture, it was constantly mixed by means of a magnetic stirrer at room temperature.

The molar ratios of reagents used for the synthesis of TiO_2 sol-gels were: H_2O: IPT = 3.75, EtOH: IPT = 21.4; 26.82 and 33.75, $HNO_{3:}$ IPT = 0.06; 0.08 and 0.18 [8].

b. EXPERIMENTAL APPARATUS

The rheological behaviour of titania sol-gels have been observed using a Rheotest 2 with 2 cylinders (Type S-S$_1$), which is based on a simple shearing flow of the sample enclosed in the gap between the 2 coaxial cylinders. From the experimental values obtained at the room temperature 20±1.5 ^{0}C, the apparent viscosity (η_{app}) was estimated on the variation of shear stress (τ) with shear rate ($\gamma = dw_x/dy$). Three replicate runs were carried out for each set of experimental conditions.

RESULTS AND DISCUSSION

The obtained data through rheological measurements, gave us information about the variation of apparent viscosity (η_{app}) during sol-gel transition for different initial rations between reagents (alcohol concentration and acid concentration) and about the variation of apparent viscosity (η_{app}) at different shear rate (γ) and at a fixed time.

Effect of alcohol concentration and acid concentration on the sol-gel evolution of titania based systems has been shown in Figure 1 and 2. Figure 1 plots the evolution of apparent viscosity (η_{app}) of titania sol-gels on the time, corresponding to different EtOH: IPT ratios. Figure 2 plots evolution of apparent viscosity (η_{app}) of titania sol-gels on the time, corresponding to different acid inhibitor concentration.

These kinds of measurements were done at a constant shear rate of 145.8 s^{-1}.

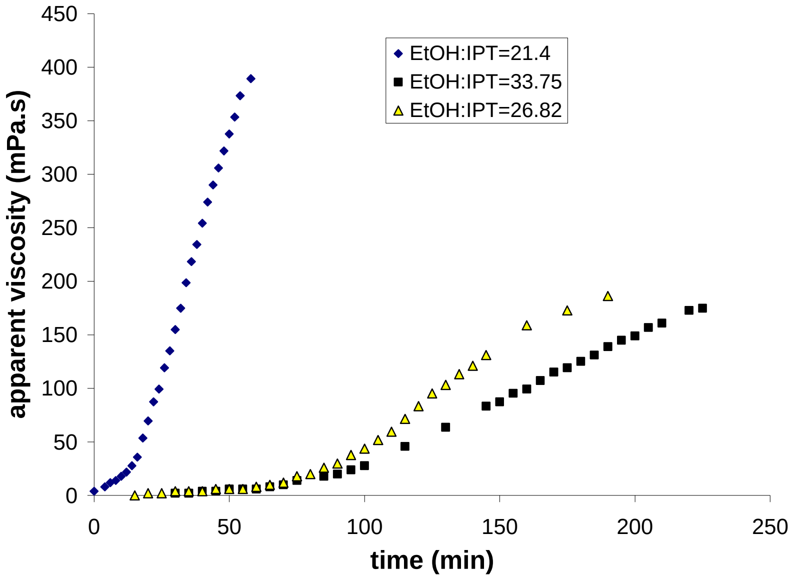

Figure 1. Effect of EtOH: IPT ratio on viscosity change versus time for titania systems during sol-gel transition.

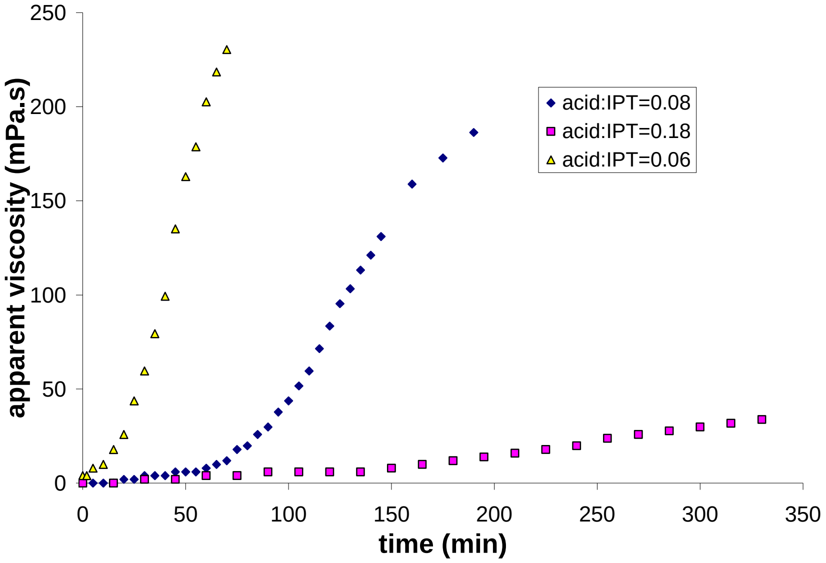

Figure 2. Effect of HNO_3: IPT ratio on viscosity change versus time for titania systems during sol-gel transition.

It is easy to see that the time of gelation for TiO_2 systems is strongly dependent on both ratios EtOH: IPT and HNO_3: IPT employed for preparing the initial solutions. For example, the gelation appears after 20 minutes in the system containing molar ratio EtOH: IPT = 21.4, and after 80 minutes in the system containing EtOH: IPT = 26.82. No substantial difference on gelation time was observed between samples having molar ratios EtOH: IPT = 26.82 and 33.75 (Figure1).

From Figure 2 it can be seen that the apparent viscosity increases quickly at low acid inhibitor concentration and very slowly at a higher concentration of acid inhibitor, a longer time until the gel structure is achieved. For the sample containing a molar ratio HNO_3: IPT = 0.18 no sudden change (increase) was observed during 350 minutes. This means that the increase of the acid inhibitor increase the gelation time, offering longer time for sol-gel transition, and thus a better control on the surface of the films (coatings) when this is necessary (Figure 2).

For the second collection of measurements, necessary to establish the behaviour of titania systems during sol-gel transition the shear rate were varied between 27 s^{-1} and 729 s^{-1}.

The results have shown that the samples used in this kind of experimental measurements (having a molar ratio EtOH: IPT = 26.82, and HNO_3: IPT = 0.08) exhibit a linear and constant, independent on shear rate, shear stress and time, evolution of apparent viscosity (Newtonian behaviour) before gelation (Figure 3), and a non-linear, pseudoplastic, non-Newtonian behaviour after gelation, proper to gel structure, and similar to other synthesised gels [6] (Figure 4).

Figure 4 plots the evolution of the apparent viscosity for two samples collected after 80 minutes that the mixing of reagents was initiated and after 100 minutes.

The analysis of curves plotted in Figure 4 have shown the decrease of apparent viscosity (η_{app}) with increasing of shear rate (γ) in both cases, which confirms non-linear, pseudoplastic or shear-thinning behaviour of titania gels (semisolid materials). This behaviour is characteristic to a specific molecular rearrangement of the system, a de-structuration of the gel, proper to the reduction of the interaction between semisolid particles with the increase of the shear rate. In the same time it is obvious that as the shear rate increases, the slope of graphs decreases.

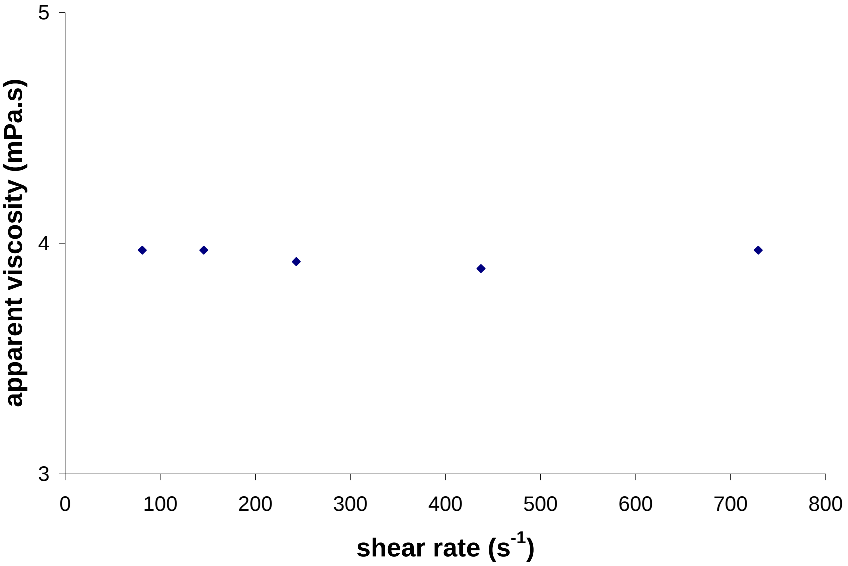

Figure 3. Behaviour of the titania sols before gelation at 30 minutes after the mixing of reagents.

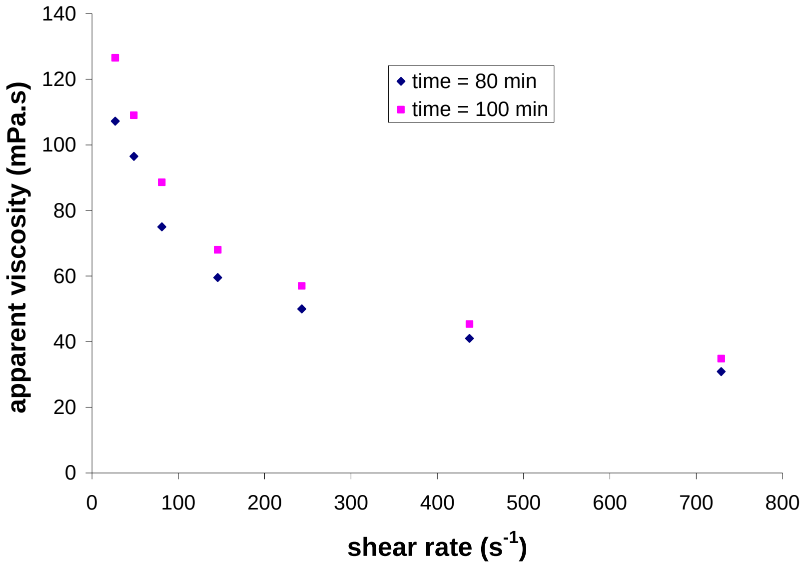

Figure 4. Apparent viscosity change with shear rate registered for the titania gel at 80 and 100 minutes after the mixing of reagents.

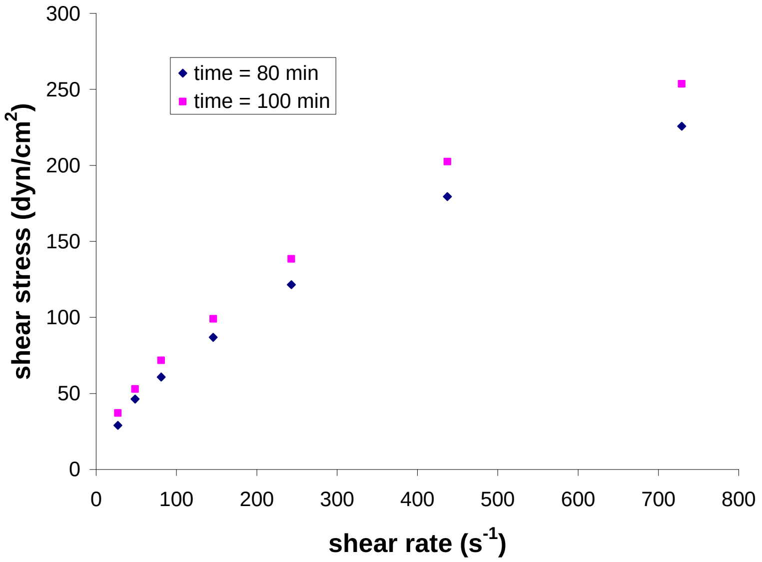

Figure 5. Shear stress (τ) versus shear rate (γ).

The specific plot obtained in Figure 5 confirms the non-Newtonian behaviour of titania systems after gelation, the decrease of the slope of graph with the increase of the shear stress.

Fitting the experimental data obtained for the gel samples to the theoretical power law model Ostwald de Waele, which describes the relationship between shear stress and shear rate (Equation 3), a value of n equal 0.62 was obtained at 80 minutes after mixing of raw solutions and a value of 0.59 at 100 minutes. The values of n index lower than unity confirms the pseudopalstic behaviour of gel samples.

$$\tau = k\gamma^{n} \tag{3}$$

where k and n are rheological constants of material.

CONCLUSIONS

In this work we have demonstrated that for the titania sol-gels the time of gelation depends on the initial ratio of reagents (EtOH: IPT and HNO_3: IPT). Rheological measurements have shown that the increase of initial concentration of ethanol and acid inhibitor has led to the increase of the time of gelation.

Through rheological measurements, which provide an easy tool for understanding the behaviour of titania based systems during sol-gel transition, the values of apparent viscosity were determined and from special plots the behaviour of the titania sols as Newtonian fluids and gels as non-Newtonian or pseudoplastic fluids was established.

The theoretical power law model Ostwald de Waele, has confirmed the behaviour of TiO_2 system during sol-gel transition.

The influence of other components (e.g., molar ratio H2O: IPT) and of the temperature on the TiO_2 sol-gel transition can be researched in a future work to determine the chemistry and the activation energy involved in this kind of processes.

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