Rheological study on the aging process in a polymeric fumed silica suspension

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ABSTRACT

Understanding the influence of storage time on the rheological properties polymeric fumed silica gels is very important in the field of composite polymer electrolytes. A rheological study of the aging process of Aerosil R805 suspension in Polypropylene Glycol Mw2000 has been carried out by means of steady and oscillatory experiments.

INTRODUCTION

Fumed silica is an amorphous, non-porous form of silicon dioxide (SiO_2) with a very low density and a powdery appearance. It is prepared by flame hydrolysis of silicon tetrachloride ($SiCl_4$) in an oxyhydrogen gas flame with the end product consisting of, typically, primary spherical particles of ~10nm in diameter and the surface areas between 100 to 400 m^2 per gram, due to the branched structure of the aggregates. These characteristics give fumed silica interesting and convenient properties as a reinforcing material, as well as thickener agents, due to its ability to create three-dimensional networks. Silanol groups are found on the surface of fumed silica particles, which are responsible for its hydrophilic behaviour (Si-OH) due to they give the possibility of interactions through hydrogen bonding not only between particles, but also with solvent media and polymers[1,2]. These silanol groups can be replaced by other functional groups, so that interactions between particles or particle-medium can be tuned. That is the case of Aerosil® R805, which has been obtained after treating fumed silica (Aerosil® A200) replacing on the particle surface partially the silanol groups by octadecylsilane chains. Due to the presence of these chemicals bounds on its surface it can no longer be wetted into water. This hydrophobic silica has found numerous applications in the most diverse sectors of industry in many areas, coating and fibre optics technology for instance, and some of them would not have been possible with hydrophilic silicas[3].

When such nanoparticles are added to a continuum phase to prepare a colloidal dispersion, three states of aggregation are likely to occur: [a)] particulates do not interact with each other (or interactions are minimal) and remain isolated, [b)] fumed silica particles form clusters or flocs, and [c)] a three dimensional network is formed by flocculation of the clusters. The first situation is known as a stable suspension and the last one is usually referred to as a gel[4]. These systems also exhibited different self-similar (fractal) structures depending on the nature of the solvent. Scaling relationships showing the dependence of elastic modulus on fractal dimension of the network and volume fraction have been proposed[5].

In this work Polypropylene Glycol Mw 2000 has been used to prepare non-aqueous suspensions of Aerosil® R805 5% v/v. The presence of octadecylsilane chemical bounds on the surfaces of silica particles may let them develop a three-dimensional network without interacting chemically with polypropylene chains. So a flocculated suspension is formed. The interest in this class of suspensions stems, for example, from its application as composite polymer electrolytes in rechargeable lithium batteries since high ionic conductivity of low molecular weight polymers can be combined

with the high mechanical properties that the fumed silica networks provide to these materials, letting design batteries for any shape and size[6-9].

The purpose of this work is to study the influence of storage time on the rheological properties of Aerosil® R805 dispersions in Polypropylene Glycol molecular weight 2000g/mol 5% v/v.

MATERIALS AND METHODS

Aerosil® R805 has been used as filler in a matrix of PPG. The specific surface area BET of this fumed silica is 150±25g/m^2. The average primary particle diameter is 12nm. It is presented as a fine white powder, with a purity of 99.8% and it was used without any additional purification process.

Polypropylene glycol shows Newtonian behaviour at room temperature. It is a polar medium with hydrogen-bonding capacity. So, the polypropylene glycol can easily form hydrogen bonds through its terminal –OH groups o internal ether group. Polypropylene Glycol Molecular weight 2000g/mol (PPG2000) has been used without any additional modification process.

The samples were prepared by adding the solvent to the fumed silica in a blender and mixing for five minutes at 400rpm. This was determined to be the minimum mixing time and velocity to ensure reproducibility between batches. They were prepared in batches of 35ml and placed afterwards under vacuum and sonication for 1h in order to remove air bubbles. The concentration of silica was 5% by volume. The solids volume fraction, which was calculated using the density of the solvent (1.00g/cm^3 for PPG2000) and the fumed silica (2.2g/cm^3), represents the volume of fumed silica would occupy if it were in a compacted state. The open structure of the fumed silica, however, renders the effective volume fraction significantly larger than this calculated value.

After preparing the batches, they were divided into two samples: one of them was studied along the same day (fresh sample) and the other one was kept in the fridge at 5ºC for 24 days (old sample) with the purpose of ensuring that no denaturalization of the polymer matrix occurs.

Steady and oscillatory experiments have been carried out in this work to characterise the behaviours of these suspensions. The rheological study was carried out with a rheometer RheoStress RS600 (Haake). A cone-plate sensor system was used, which a diameter of 35 mm and an angle of the cone of 2º. All the experiments were carried out at 25.00±0.05ºC.

It is well known the thixotropic behaviour of fumed silica suspensions in other polymers. Therefore, these suspensions may present preshear history dependent behaviour. In order to make sure the results of the experiments will be reproducible, previous to the experiment the sample is undergone to a preshear stage at a certain shear rate value until it achieves a steady state in these conditions[10,11]. This value of shear rate has been previously determined and it is the highest value of shear rate which let the system keeps its reversibility. In this way, we ensure that the previous shear history had been eliminated and the reversibility of the sample was conserved. After that preshear stage, the sample was left at rest for 300s in order to let the system develop an initial structure level. For fresh samples the maximum shear rate value which keeps the reversibility of the system up to a 90% is 10s^{-1}, while for old samples it is 2.5s^{-1}.

RESULTS

Viscosity Curve

The viscosity curve gives the equilibrium viscosity value at any shear rate. Both samples show shear thinning behaviour, as it can be observed from Fig.1. It can be seen that both fresh and old samples exhibit almost the same behaviour, since their viscosity curves almost overlap one to each other.

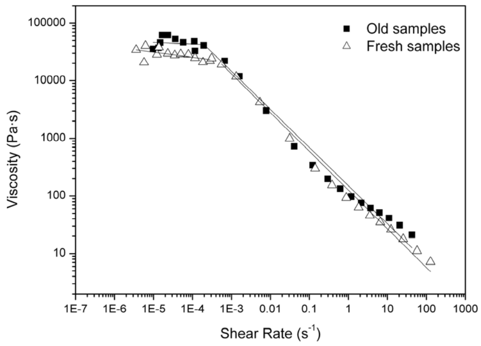

Figure 1. Viscosity curve and power-law fittings.

So there are two ranges of behaviour, one for shear rates lower than the deflecting point $(\dot{\gamma}_d, \eta_d)$, and another for higher values. In both ranges they follow a power-law tendency, see Eq. 1, where k is called *consistency* and n is the power-law index, establishing the dependence with shear rate.

$$\eta = k \cdot \dot{\gamma}^{n-1} \qquad (1)$$

Table 1 contains the power-law parameters which come from fitting Eq. 1 to each one of the slopes in viscosity curves.

Table 1. Power-law parameters.

Sample	K	n
Fresh ($\dot{\gamma} < \dot{\gamma}_d$)	11200±14	0.911±0.001
Fresh ($\dot{\gamma} > \dot{\gamma}_d$)	126.3±0.2	0.328±0.003
Old ($\dot{\gamma} < \dot{\gamma}_d$)	34080±5	0.974±0.002
Old ($\dot{\gamma} > \dot{\gamma}_d$)	150.41±0.04	0.338±0.001

Although they have shear thinning behaviour with two slopes, they differ slightly in the deflecting point, as well as the parameters of fitting (see Table 1). Both samples show a first slope with a value for n close to 1, so at very low shear rates their behaviour is close to Newtonian so it can be said that in this range it has almost non dependence with shear rate. For shear rates higher than the deflecting point they exhibit a power-law index value rather far away from 1, being slightly higher for the old sample.

It is not a weird result, because the chemical nature of silica and suspending media is the same for both samples, so that the energy of the links formed between silica particles might be almost the same and, consequently, the rate of breaking them down as well. The fact of having a value for n rather different to 1 confirms they have a noticeable shear thinning behaviour.

Related to consistency, the value for the old sample is higher than for the fresh one and it might be a consequence of the presence of a more widespread network, due to the fact of having more time to develop the structure.

Transient states

As it has been already described, the silica particles form a network inside the polymer matrix which can breakdown and rebuild-up, depending on the applied shear rate at which and the structure level developed at each moment. So it seems rather possible that this process of breaking-down and building up might be time dependent. In order to check whether there really is or not a time dependence step-wise experiments have been carried out. As it is well known, fumed silica exhibits thixotropy in other suspending media, so it seems interesting to study if inside the range of reversibility in shear rate it really shows this behaviour or not. However, with the purpose of highlighting the effect of aging, the same step-wise experiment has been developed.

So, three steps have been applied consecutively: From 0 to 0.1s^{-1}, from 0.1 to 5s^{-1} and from 5 to 0.1s^{-1}.

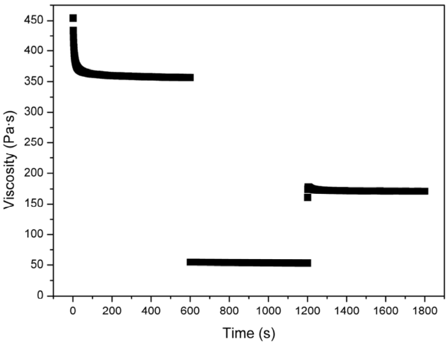

Figure 2. Old samples' answer for step-wise experiments.

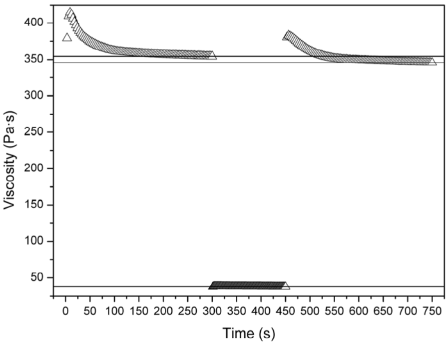

Figure3. Fresh samples' answer for step-wise experiments.

As it can be observed (Figs.2 and 3), both samples exhibit time dependent behaviour, although there two an important differences between them: The first one is that the old ones are not reversible when they are undergone 10s^{-1}; and the second one is that the old ones, under the effect of the first step, they do not exhibit an elastic answer.

Stress sweep

Stress sweep lets determine de limit of the linear viscoelastic (LVE) region at a certain frequency value. In all samples at any frequency, the storage modulus (G') leave being linear at lower values for shear stress than the loss modulus (G''), so it is considered to calculate this limit for LVE. As it can observed in data from Table 2, the older the sample is, the higher the shear stress that the system can suffer keeping its linear behaviour and the higher the values for G' are. This result agrees with the analysis done for the results given by the step-wise experiment, the old samples have more solid like behaviour.

Table 2. Values for the limit of LVE region at 1rad/s.

Sample	τ_{LVE} (Pa)	G' (Pa)
Old	3.38	2934
Fresh	2.87	1271.43

Both samples have a critic value for shear stress in which a transition sol-gel occurs and G'' is over G' and the viscous behaviour is dominant. This critic value is higher for fresher samples.

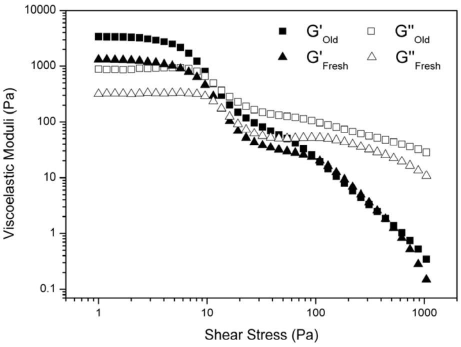

Figure 4. Shear Stress value for the limit of LVE region at 1rad/s.

Frequency sweep

This is an oscillatory test with variable frequency and constant shear stress value, selected inside the LVE range, so in both samples the elastic behaviour (G'>G'') dominates over the viscous, showing gel character. It can be seen in Fig.5 that both systems exhibit the same shape for their curves, having higher values for viscoelastic moduli the old one (see Fig. 5). This result also agrees with the previous ones.

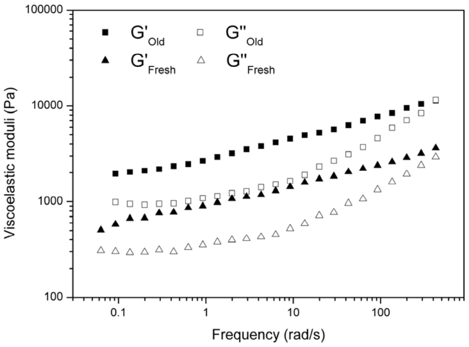

Figure 5. Frequency sweep experiment inside the LVE.

Previous studies[12] have stated that silica particles aggregate following a fractal order. The fractal dimension (d_f) can be calculated from the results obtained with frequency sweep experiments.

Complex viscoelastic modulus (G*) depends on frequency following a power law equation (see Eq. 3 and Fig.6).

$$G^* = G^*_0 \cdot \omega^n \quad (2)$$

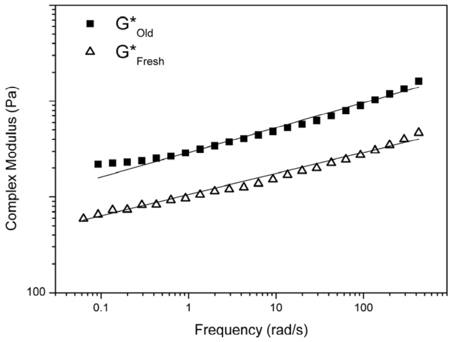

Figure 6. Complex modulus Vs frequency.

Table 3. Power law fitting parameters and fractal dimension.

Sample	G^*_0(Pa)	n	d_f
Fresh	1057.08	0.220	1.431
Old	2916.6	0.258	1.418

The exponent n of the power law equation (Eq.2) can be related to the fractal dimension d_f by the Eq.3.

$$n = \frac{d\left(d+2-2d_f\right)}{2\left(d+2-d_f\right)} \quad (3)$$

Where d denotes the space dimension (d=3 for a three dimensional network).

So fractal dimension for each sample has been calculated (Table 3). A lower value for this parameter implies a more open structure. However, in this case it seems that there are almost no differences in the kind of fractal aggregation.

CONCLUSIONS

The influence of storage time on dispersions of Aerosil® R805 in PPG2000 has been studied. Both samples have gel appearance at rest, which means that silica particles have developed a three dimensional network inside the polymer matrix. In order to determine the properties and differences between them, they have been undergone to steady and oscillatory experiments. All results agree with the idea of the longer the storage time, the more developed the structure is.

ACKNOWLEDGMENTS

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