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The influence of the suspending phase on the rheological behaviour of Aerosil R805 suspensions

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ABSTRACT

The influence of length of the chains in the liquid phase (Polypropylene Glycol) on the rheological properties of Aerosil R805 suspensions has been studied using steady and oscillatory experiments and, it has been concluded that he shorter the chains are, the stronger the network formed by the filler is.

INTRODUCTION

Colloidal silicas are used as fillers in various industrial applications to control rheological properties[1]. They come in a wide range of sizes and with a variety of surface treatments. The considerable specific surface area of these particles and the presence of functional chains (silanol, siloxane) play a major role in their rheological behaviour. Siloxane and silanol groups are found on the surface of fumed silica particles, which are responsible for its hydrophilic behaviour[2]. However, after treating it with silane its surface can be modified, for example attaching octadecylsilane on it and replacing most of siloxane and silanol groups, as is the case of Aerosil® R805. 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 silica[3].

The presence of octadecylsilane chemical bounds on the surface of silica particles may let them develop a three-dimensional network without interacting chemically with polypropylene chains. So a flocculated suspension is formed[4]. The interest in this class of materials stems, for example, from its application as composite polymer electrolytes in rechargeable lithium batteries, letting design batteries for any shape and size[5-7].

It is assumed that the capacity to form a three-dimensional network responsible for the formation of a gel phase depends on the volume fraction and type of colloidal silica (type of surface groups), as well as the nature of the suspending phase. In this work the first and second of these factors have been kept unaltered in all the experiments; however the length of the chains in the liquid phase has been varied with the purpose of studying its influence on the degree of network formation and its rheological behaviour.

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. This material 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. In order to determine the influence of the length of polymer chains on the rheological behaviour of suspensions, two polypropylene glycol media with different molecular weight have been used: Polypropylene Glycol Molecular weight 2000 (PPG2000) and Polypropylene Glycol Molecular weight 400 (PPG400). The ratio between their lengths is 5/1, having PPG2000 lengths of chains five times longer than PPG400. Due to this circumstance, their viscosities are different one from each other: 0.1 Pa·s for PPG400 and 0.45 Pa·s for PPG2000. Both of them have 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 densities of the solvents (1.00g/cm^3 for PPG2000 and 1.01g/cm^3 for PPG400) 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.

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, with 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[8,9]. 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 were sure 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. In the case of PPG400 suspensions, the maximum shear rate value which keeps the reversibility of the system up to a 90% is 5s^{-1}, meanwhile for PPG2000 it is 10s^{-1} (Fig. 1).

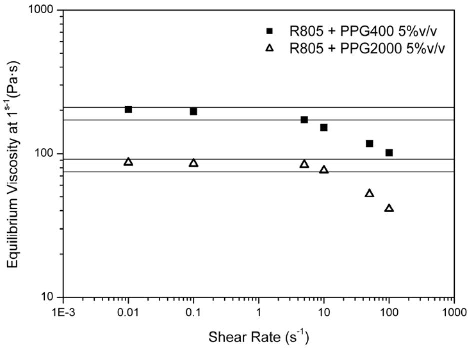

Figure 1. The limit of reversibility. The data correspond to the equilibrium viscosity at a shear rate of 1s^{-1}, after a step from the different initial shear rates, which are showed in the X-axis

RESULTS

The first result that must be analysed and discussed is the one related to the limit of reversibility (Fig. 1). As it can be observed, both suspending media increase their viscosities due to the presence of R805 particles and they are no longer Newtonian, because their viscosities depend on shear rate. Although the viscosity of PPG400 is lower than the viscosity of PPG2000 respectively, the suspension of Aerosil R805 in PPG400 has a higher equilibrium viscosity than in PPG2000 at $1s^{-1}$. However, its limit of reversibility is smaller. This information can be interpreted as the structure formed by R805 in PPG400 is stronger than in PPG2000, because its equilibrium viscosity is higher, but at the same time it is not able to recover its original state when it is sheared at shear rate values over $5s^{-1}$.

In order to get more information about the influence of the length of the polymer chains, some additional experiments have been carried out.

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 in Fig.2. The curve given for R805 in PPG400 is over the one for PPG2000, what agrees with the previous result (Fig.1).

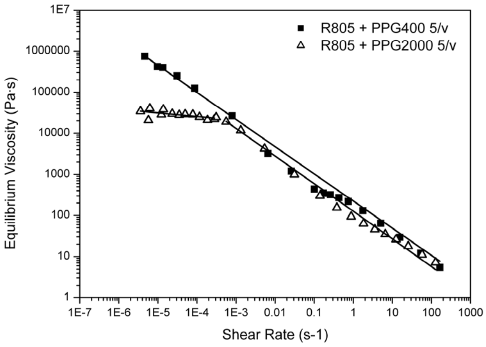

Figure 2. Viscosity curve and power-law fittings.

More over, the PPG400 exhibits only one slope in its curve, meanwhile PPG2000 shows two slopes, being the deflecting point at $5\cdot10^{-3}s^{-1}$. All of them 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.

$$\eta = k\cdot\dot{\gamma}^{n-1} \tag{1}$$

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.

Polymer matrix	k	n
PPG400	224.3±0.1	0.339±0.002
PPG2000 $(\dot{\gamma} < 5\cdot10^{-3}s^{-1})$	11200±14	0.911±0.001
PPG2000 $(\dot{\gamma} \geq 5\cdot10^{-3}s^{-1})$	126.3±0.2	0.328±0.003

The first of the slopes for R805 in PPG2000 shows a value for n close to 1, so at very low shear rates its 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 $5\cdot10^{-3}s^{-1}$ it exhibits a power-law index value very close to the one for PPG400 and rather far away from 1. 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 PPG400 sample is higher than for PPG2000 one and it might be a consequence of the presence of a more widespread network, that is the fact of shorter polymer chains let silica particles interact easily and, therefore, the three dimensional network formed is more spreaded out. Having longer polymer chains implies the particles arrange in clusters that hardly can be attached to others, so the network will not be such outstretched. So in the case of PPG2000 samples the network is not as much developed as in the case of PPG400 and the viscosity curve is close to Newtonian at very low shear rates. It might be due to silica particles form clusters not connected to others (they are almost indiviual) and at very low shear rate are almost unbreakable; therefore the viscosity is not shear rate dependent and there is a increase of the viscosity with regards to the pure PPG2000 by the presence of the clusters, which disturb the flow.

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. So, three steps have been applied consecutively: From 0 to 0.1s^{-1}, from 0.1 to $\dot{\gamma}_{\max}/2\,\mathrm{s}^{-1}$ and from $\dot{\gamma}_{\max}/2$ to 0.1s^{-1}, being $\dot{\gamma}_{\max}$ the shear rate value for the limit of reversibility.

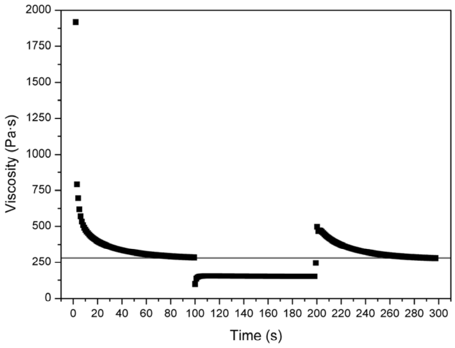

Figure 3. R805 in PPG400 5%v/v. Answer for step-wise experiments.

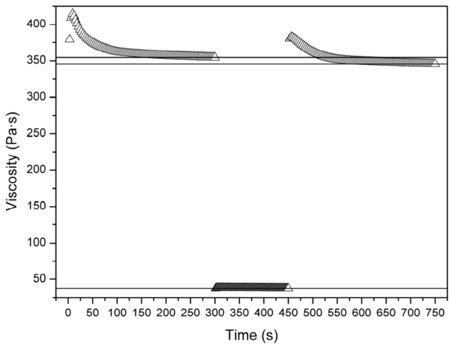

Figure 4. R805 in PPG2000 5%v/v. Answer for step-wise experiments.

As it can be observed (Figs.3 and 4), both samples exhibit time dependent behaviour and their reversibility is higher than 90%. So it may remind one a thixotropic behaviour. However, the transitory evolution of the viscosity in the third step could bring up some doubts about if it really is a thixotropic behaviour, because the shape of the curve (the answer for a step down) is qualitatively similar to the one given for the first step, which is given as a result of a step up in shear rate. Nevertheless, from a indirect microstructural approach, the most generic kinetics equation given for thixotropy[10,11] (Eq. 2) makes possible this time evolution for the viscosity in the third step.

$$\frac{d\lambda}{dt}=\frac{\alpha}{\dot{\gamma}^{a}}\cdot(1-\lambda)^{b}-\beta\cdot\dot{\gamma}^{c}\cdot\lambda^{d} \qquad (2)$$

Where λ is a structural parameter related to the flocculation level inside the material.

Moreover, there is an important difference between them. For PPG400 suspension it seems to not having such a big elastic component as for PPG2000, because at the first step up it has no overshot. In order to check this, oscillatory experiments have been carried out.

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 higher the frequency is, the higher the shear stress that the system can suffer keeping its linear behaviour and the higher the values for G'. In any case, PPG400 suspensions have higher values for G' than PPG2000 samples. This result agrees with the analysis done for the results given by the step-wise experiment, the elastic component is higher for PPG400 suspensions.

Table 2. Values for the limit of LVE region at a certain frequency value.

Polymer Matrix	Ω (rad/s)	τ_{LVE} (Pa)	G' (Pa)
PPG400	1	4.78	14335
	10	5.23	18190
	100	10.32	20017
PPG2000	1	2.37	1115
	10	4.02	1451
	100	8.05	2212

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 PPG400 samples. All this information obtained from stress sweep experiments agrees with the idea a stronger network for this system extracted by the already commented results.

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. The purpose of this experiment is to determine the stability of dispersions and the fractal dimension of the structures developed.

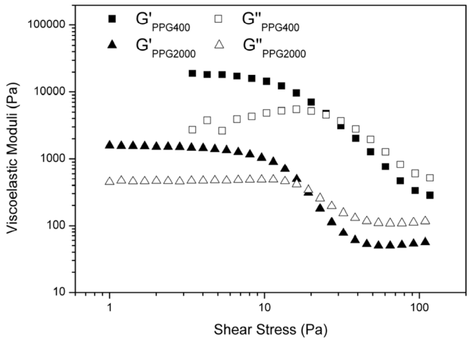

Figure 4. Shear Stress value for the limit of LVE region at 10rad/s.

It can be seen in Fig.5 that both systems are stable dispersions, since G' and G'' curves are almost parallel straight lines through the entire frequency range[12] (see Fig. 5).

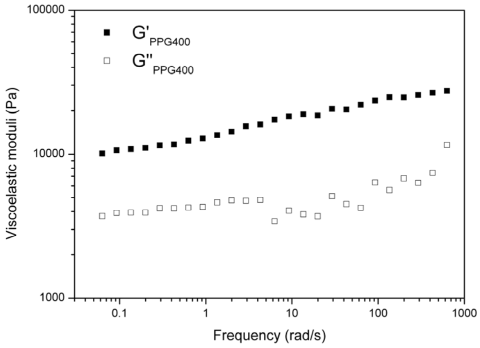

Figure 5. PPG400 answer for a frequency sweep experiment inside the LVE .

Previous studies[13] 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).

$$G^* = G^*_0 \cdot \omega^n \qquad (3)$$

The exponent n of the power law equation (Eq.3) can be related to the fractal dimension d_f by the Eq.4[13].

Table 3. Power law fitting parameters and fractal dimension.

Polymer Matrix	G^*_0(Pa)	n	d_f
PPG400	14172.9	0.1134	1.4652
PPG2000	1057.1	0.2203	1.4309

$$n = \frac{d\left(d + 2 - 2d_f\right)}{2\left(d + 2 - d_f\right)} \tag{4}$$

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

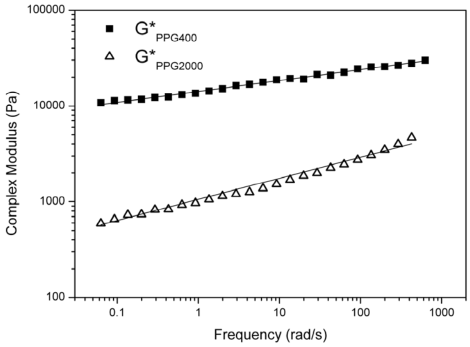

Figure 6. PPG400 and PPG2000 answer for a frequency sweep experiment. Complex modulus fitted by Eq. 3.

So fractal dimension for each sample has been calculated (Table 3). A lower value for this parameter implies a more open structure. Therefore, R805 forms a more opened network in PPG2000 than in PPG400. The reason for that must be found in the fact of the longer the polymer chains are, the more difficult is the interaction between the clusters and consequently the formation of the network is more open.

CONCLUSIONS

Dispersions of Aerosil® R805 in PPG400 and PPG2000 have 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 chains of the polymer are, more difficult is the interaction between the clusters and consequently the formation of the network is more open, what implies weaker mechanical properties.

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