

STATIC AND DYNAMIC YIELD STRESSES OF AEROSIL® 200 SUSPENSIONS IN POLYPROPYLENE GLYCOL

F.J. GALINDO-ROSALES^{1*} AND F. J. RUBIO-HERNANDEZ²

¹Department of Mechanical Engineering and Mining, University of Jaen, 23071 Jaen, Spain

²Department of Applied Physics II, University of Malaga, 29071 Malaga, Spain

* present address: Department of Chemical Engineering,
Katholieke Universiteit Leuven, 3001 Heverlee, Belgium

* Email: curro@galindorosales.com

Fax: x34.951952514

Received: 19.4.2009, Final version: 18.8.2009

ABSTRACT:

Fumed silica suspensions in low molecular weight liquids are used in many photonic and microelectronic applications, playing its rheology a major role in the effectiveness of their usage. Particle-particle and particle-liquid medium interactions of suspensions of hydrophilic fumed silica in low molecular weight polar media, polypropylene glycol of 400 and 750 g/mol, concretely, have been already investigated. There, the affinity between polar solvent molecules and fumed silica particles prevents the formation of a 3D gel network. In this work it has been found that fumed silica can develop a flocculated suspension when it is dispersed in polypropylene glycol with a molecular weight of 2000 g/mol. Besides, it has been found that this suspension exhibits time dependent behaviour within its reversible shear thinning region, which is related to thixoelectricity. The experimental method, proposed theoretically by Cheng in 1986 to obtain the dynamic yield stress in thixotropic systems has been here extended successfully to a thixoelectric system.

ZUSAMMENFASSUNG:

Suspensionen aus Quarzstaub in niedermolekularen Flüssigkeiten werden in vielen photonischen und mikroelektronischen Anwendungen verwendet. Dabei spielen die rheologischen Eigenschaften eine wesentliche Rolle hinsichtlich der Anwendungseigenschaften. Partikel-Partikel- und Partikel-Matrix-Wechselwirkungen in Suspensionen von hydrophilem Quarzstaub in niedermolekularen polaren Medien (Polypropylenglykol mit einem Molekulargewicht von 400 bzw. 750 g/mol) wurden untersucht. In diesen Systemen verhindert die Affinität zwischen den polaren Lösungsmittelmolekülen und den Quarzstaubpartikeln die Bildung eines dreidimensionalen Gelnetzwerkes. In dieser Arbeit wird gezeigt, dass Quarzstaub eine ausgeflockte Suspension bildet, wenn es in Polypropylenglykol mit einem Molekulargewicht von 2000 g/mol dispergiert wird. Darüber hinaus wurde gefunden, dass die Suspension ein zeitabhängiges Verhalten innerhalb des reversiblen Bereiches der Scherverdünnung aufweist, das im Zusammenhang mit Thixoelektrizität steht. Die experimentelle Methode, deren theoretischer Ansatz von Cheng 1986 vorgeschlagen wurde, um die dynamische Fließspannung in thixotropen Systemen zu messen, wurde hier erfolgreich auf thixoelektrische Systeme übertragen.

RÉSUMÉ:

Les suspensions de silice fumée dans des liquides de bas poids moléculaire sont utilisées dans de nombreuses applications en photonique et microélectronique. Leurs propriétés rhéologiques jouent un rôle majeur dans les performances d'utilisation de ces suspensions. Les interactions particule-particule et milieu liquide-particule dans des suspensions de silice fumée hydrophiles dans du polypropylène glycol de 400 et 750 g/mol ont été étudiées en particulier. Dans ce cas, l'affinité entre les molécules de solvant polaire et les particules de silice fumée empêchent la formation d'un réseau 3D géifiant. Dans de travail, on a trouvé que la silice fumée peut développer une suspension flocculée quand elle est dispersée dans du polypropylène glycol de masse moléculaire de 2000 g/mol. En revanche, il s'avère que cette suspension présente un comportement qui dépend du temps dans sa région rhéo-amincissante réversible, qui est due à la thixoelectricité. La méthode expérimentale proposée en théorie par Cheng en 1986 afin d'obtenir une contrainte seuil dynamique dans les systèmes thixotropiques, a été ici étendue avec succès à un système thixoelectrique.

KEY WORDS: fumed silica, static yield stress, dynamic yield stress, thixotropy, colloidal suspension

1 INTRODUCTION

Fumed silica is amorphous nonporous silica prepared by a flame hydrolysis of SiCl_4 . Its surface chemistry is hydrophilic due to the presence of hydroxyl or silanol groups (-OH) on the surface. These groups let particles link each other in liquids by means of hydrogen bonding and are responsible of its ability to form network structures. This is the mainly reason why fumed silica systems are widespread used in emerging technologies, like photonics and microelectronics. To achieve the expected result in the final product, it is sometimes necessary using an organic media as a liquid phase. However, Raghavan et al. [1, 2] found that hydrophilic fumed silica is largely incapable of gelling polar organic liquids with low molecular weight (< 750 g/mol), just because medium molecules preferentially form hydrogen bonds with the surface silanol groups present on the silica aggregates. Thereby, it is expected that these suspensions were non-flocculated and, consequently, its yield stress (YS) will be extremely low. As the YS is a rheological parameter with evident implications in the process engineering, an understanding of the rheology of fumed silica in polar organic liquids is critical to maintain the integrity and reliability of the final product [1, 2].

Theoretically the YS is defined to be the stress at which the fluid just starts/stops moving, in other words, when the viscosity changes between being finite and infinite. This definition of YS is inapplicable for experimentalists, because experiments of infinite duration would be required in order to distinguish between finite and infinite viscosities. Consequently, the measured yield stress may depend on the patience of the experimentalist and the experimental protocol. So, depending on the experimental procedure quite different values of YS can be obtained [3 - 5]. However, despite of the controversial concept of the YS as a true material property, its usefulness in engineering design and operation of processes when handling and transport of industrial suspensions are involved make YS an important parameter from a practical point of view. One method that has been used for such applications is to work with two yield stresses, one static and one dynamic [6].

As a consequence of the structure formation, it has been pointed out [7] that it is possible to distinguish between the Static Yield Stress

(SYS) and the Dynamic Yield Stress (DYS) in thixotropic materials. The SYS can be experimentally obtained by applying a quick (non-equilibrium) shear stress ramp to the system. The idea in which is based upon this rheological test is that, starting from rest state, the sample will eventually start to flow by increasing the applied shear stress, just when a critical shear stress value was exceeded. The DHS is obtained from the steady-state flow curve (SSFC). The steady-shear stress value, obtained from the extrapolation of the SSFC in the limit $\dot{\gamma} \rightarrow 0$, is assumed as the DHS [7]. Hence, while the SYS is related to the amount of stress necessary to get the test material starts to flow from a rest state (i.e. it is an indication of the transformation from a solid state to a viscoplastic state), the DHS can be understood as the stress necessary for stopping a flowing test material (i.e. it is an indication of the transformation from a viscoplastic state back to the solid state). As an example of the practical utility of the separation in both YS values, the DHS is considered as the parameter responsible for stopping the flowing concrete inside the mould or framework, while it is necessary to know the SYS of the concrete to select an adequate concrete pump [8]. On the other hand, the existence of different SYS and DHS values in the same material is taken as an indication of that more than one kind of structure exist in the system [7]. Following Cheng, one of these structures would be very sensitive and would be broken down by relatively small shear values and it would only be built up at rest, while the other one would be more robust and would withstand moderate shear rates being responsible for the DHS. The SYS is consequence of the combined structure. Therefore its value will be higher than the DHS one [9].

Surveying the literature it can be found a different definition for the term "dynamic yield stress". It can be defined as the stress value at which deviation from linearity occurred in oscillatory stress sweep tests. This definition has been used to determine the yield stress of emulsions and the term "dynamic" appears because of the fact that this parameter is obtained by means of an oscillatory test. However this definition of dynamic yield stress is not constant but strongly dependent on frequency; besides, it does not present reasonable correlation with the yield stress estimated from flow curves [10]. Therefore, here this definition of dynamic yield stress will not be considered.

Physical property	PPG400	PPG2000
M_w [g/mol]	400	2000
ρ [g/cm ³]	1.01	1
$\eta_{20^\circ\text{C}}$ [Pa·s]	100	450
R_g [Å]	7.8	54

Table 1:
Physical-chemical properties
of PPG400 and PPG2000

In this work it has been found that the length of polypropylene glycol molecules has an important effect on the effectiveness of the solvation of Aerosil® 200 particles. Then, when these molecules are long enough, they cannot prevent that silica particles link each other anymore and, consequently a network would be formed. The presence of a network would imply higher values of YS and, possibly, time dependent behaviour. If time dependence were related to thixotropy, according to Cheng, it would be possible distinguishing between SYS and DYS. This paper presents a study of the influence of the length of the polypropylene glycol molecules on the microstructure of Aerosil® 200 suspensions by using rheometrics. Discrimination between flocculated and non-flocculated suspensions has been made by means of steady and oscillatory tests. In the case of flocculated suspension, the YS and time dependent behaviour due to thixoelectricity has been determined. Finally, SYS and DYS have been calculated following the rheological experiments described above. This allows an analysis of the microstructure formed by Aerosil® 200 particles when they are dispersed in a relatively high molecular weight polar medium

2 MATERIALS AND METHODS

In this work Aerosil® 200 supplied by Degussa A.G. (Düsseldorf, Germany) has been used as hydrophilic fumed silica, whose character is given by keeping the whole original silanol (Si-OH) groups on its surface. This material is presented as a fine white powder with a purity of 99.8 %, and was used without any additional purification process. Its specific surface area BET is $\approx 200 \pm 25$ m²/g and its primary spherical particles average size is 12 nm [11-13]. However, although the flame hydrolysis process initially produces spherical particles, as they are hot at the end of the production process the particles collide each other and they fuse into aggregates. These aggregates are branched, fractal structures, and can be considered as fumed silica primary structure since the fusion process is irreversible and they cannot be separated by shear [14]. The continuous phase here considered is polypropylene glycol (HO-[CH₂-CH(CH₃)-O]_n-H) with two different molecular weights, 400 g/mol (PPG400) and 2000 g/mol (PPG2000) on average (Sigma-Aldrich Chemical GmbH, Düsseldorf, Germany). Both have low and constant viscosity under ambient

conditions. Some of their physical-chemical properties are included into Table 1.

Each suspension was prepared by adding the liquid to the silica and afterwards mixed in a blender for 10 minutes at 796 rpm. These parameters have been determined, in a previous study, as the minimum mixing time and angular velocity required to ensure homogeneity and reproducibility between batches. Samples were made in batches of 35 cm³ and placed under vacuum and sonication conditions at room temperature for one hour in order to remove air bubbles. Afterwards the sample was let at rest for 12 h in an airtight plastic bottle. The volume fraction of Aerosil® 200 particles in the suspensions is quite low $\phi_s = 0.05$, calculated from bulk densities considering silica particles as Euclidean solids, which corresponds to the 10.378 and 10.286 %w/w for PPG400 and PPG2000 suspensions, respectively. To sum up, both samples were composed by the same kind of particles, which particle size distribution and shape are identical. Even the chemical interactions with the suspending media are of the same kind, i.e. the silanol groups on the surface of the silica particles form hydrogen bonds with the polymer chains of PPG. So the only difference between them is related to the length of the polymer molecules of the suspending media.

All rheological experiments were carried out at $25.0 \pm 0.1^\circ\text{C}$, with a controlled temperature bath (Thermo Haake DC30), on a Rheostress RS600 (Haake Thermo Electron Corporation GmbH, Karlsruhe, Germany), using a cone-plate sensor system with a cone angle of 2° and a diameter of 35 mm. Experiments were conducted under both steady as well as dynamic oscillatory shear. The time dependent behaviour of fumed silica suspensions is well known. Therefore, it is a common practice applying a pre-shear stage in order to erase this pre-shear history dependent behaviour [15-19]. So, in order to ensure the results were reproducible, before each experiment, a steady pre-shear was applied up to an equilibrium state ($d\tau(t)/dt \leq 0.01$ Pa/s). In this way, any previous shear history on the sample was erased [20]. The value of the shear rate applied in this pre-shear stage is the limit of reversibility of the sample in order to ensure that they have not been denatured [21]. Afterwards, the sample was kept at rest for a period of time long enough to let them achieve an equilibrium structure [22].

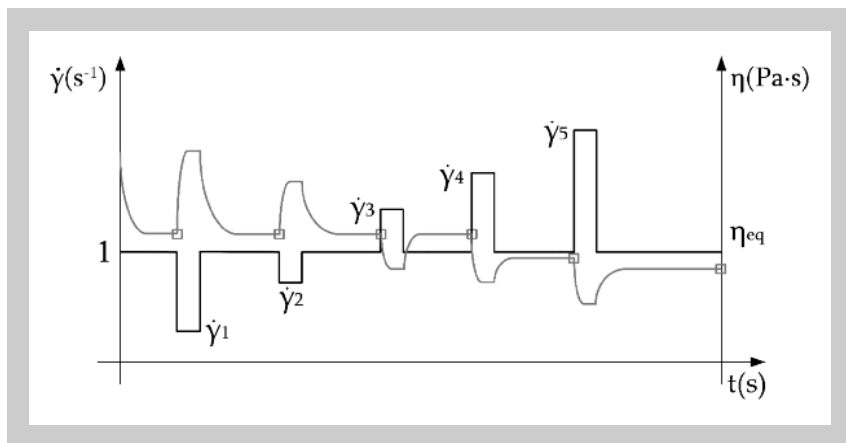


Figure 1 (left): Scheme of the experimental protocol followed to obtain the limit of reversibility.

Figure 2: Limit of reversibility for A200 suspensions in PPG400 and PPG2000 at 5 %v/v.

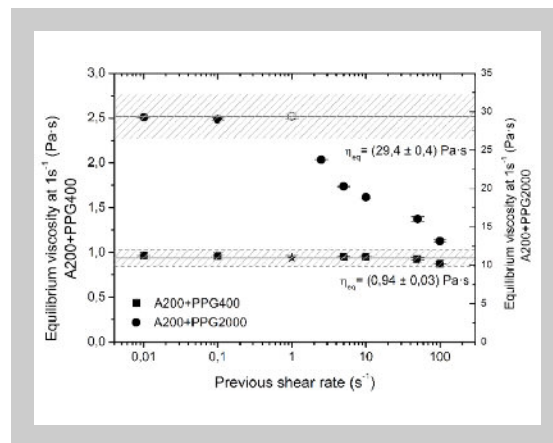
2.1 LIMIT OF REVERSIBILITY

The limit of reversibility has been defined as the maximum shear rate value that a sample is able to suffer without losing its original properties [21]. To determine this limit, the samples here studied have been sheared at 1 s^{-1} until the equilibrium in the apparent viscosity (η_m) is achieved. After this, a step wise in shear rate is applied at $\dot{\gamma}_i$ during 300 s. Then it is undergone to 1 s^{-1} up to the equilibrium is reached again. The values fixed for $\dot{\gamma}_i$ were $0.01, 0.1, 5, 10$ and 100 s^{-1} (Figure 1). The limit of reversibility of each sample was determined comparing the apparent viscosity equilibrium values each time that the sample was again sheared at 1 s^{-1} . The maximum shear rate $\dot{\gamma}_i$ after which the sample is able to recover the 90 % of the η_{eq} -value at 1 s^{-1} , is the limit of reversibility. In Figure 2 it can be observed that suspension of A200 in PPG400 is reversible up to 100 s^{-1} , whereas in PPG2000 is only up to 1 s^{-1} .

2.2 RESTING TIME

Taking into account that the microstructure of the suspension is due to the agglomerates or flocs formation between primary particle aggregates, which link each other by hydrogen bonds, it can be assumed that the bigger the agglomerates' size is, the more amount of these bonds are present and consequently, the stronger the microstructure will be. On the other hand, the strength of a microstructure can be measured as the shear stress response at a certain applied shear rate.

As the resting time may logically influence in the final size of the agglomerates, it is necessary to determine the time needed to achieve the equilibrium structure at rest for each sample. To determine the minimum time interval in which the equilibrium structure is achieved, stepwise tests have been carried out after different resting times at a low shear rate ($\dot{\gamma} = 0.1 \text{ s}^{-1}$). In Figure 3 it can be seen that in PPG400 suspension only needed 60 s to develop its equilibrium microstructure because longer resting times result in the same shear stress response of the sample.



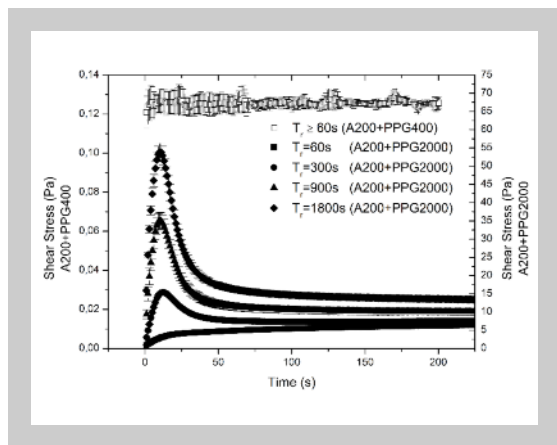
Therefore, the biggest agglomerates' size of Aerosil® 200 particles in PPG400 is formed just in 60 s of resting time. However, in PPG2000 suspension longer times let Aerosil® 200 particles reach each other and form bigger agglomerates. It is needed at least 1800 s to develop the greatest size of agglomerates and then the maximum structure level. Summing up, it has been determined that the equilibrium structure is achieved after 60 s of rest stage for PPG400 suspension and after 1800 s for PPG2000 one. These resting times will be considered for this stage in the protocol of the experiments.

2.3 PROTOCOLS OF EXPERIMENTS

Finally, the protocols for the rheological experiments we have made with both suspensions consist of three stages. The first one is the pre-shear, the second one is the rest period, and the third one is the rheological test itself. In the next section the experimental results are exposed sorted into steady and dynamic experiments.

3 RESULTS AND DISCUSSION

The steady viscosity curve was obtained by applying an increasing series of discrete shear rate steps. Each point of the plot has been obtained after shearing the sample at a certain shear rate until the equilibrium stress response was obtained ($d\tau(t)/dt \leq 0.01 \text{ Pa/s}$). Figure 4a shows suspension of Aerosil® 200 in polypropylene glycol 400 g/mol exhibiting shear thickening behaviour in the middle of shear rate range considered. So, it can be considered that this system is non-flocculated. The slight shear thinning behaviour at low shear rates can be due to the breakdown of the bigger aggregates into smaller ones. As these aggregates are not connected each other, there is not a network and the suspension is non-flocculated. On the other hand the suspension in PPG2000, as it presents shear thinning in the whole shear rate range considered (Figure 4b), presumably due to the breakdown of a three dimensional network, is as-



sumed as flocculated [1, 2, 22]. Therefore, it is obvious that the length of the polymer molecule has a great influence on the microstructure developed by A200. In order to understand why A200 is able to develop a 3D network in PPG2000, but not in PPG400, it is needed to focus on the particle-particle and particle-media interactions.

Khan and Zoeller [22], and Raghavan et al. [2] found out that A200 in polar media with low molecular weight (< 750 g/mol) is unable to develop a volume filling network structure and then these systems are not flocculated. They deduced that particles of A200 present a preferential interaction with liquid molecules, because preserving the whole original silanol groups they form hydrogen bonds with the polymer molecules, and this would lead to a solvation layer that coats each silica particle of each primary aggregate. Following their argument, as the length of polymer chains is, according to the information given by the fabricant, approximately five times shorter than particle's diameter in the case of PPG400 suspension (Table 1), the solvation of the silica particles is almost whole effective and, consequently, it is expected that only few particle primary aggregates form agglomerates. The disruption of these agglomerates under shear would justify the existence of the reversible shear-thinning region found at shear rates lower than 10.91 s^{-1} . Due to the effective solvation of the silica particles by PPG400 molecules, the particle-particle interaction will be short-range order and this system is non-flocculated. As it has been described, this proposed scheme is consistent with the given result of the steady viscosity curve. The slight shear thinning region at low shear rates, lower than critical shear rate ($\dot{\gamma} \leq \dot{\gamma}_c$), occurs because the mechanical energy applied is able to disrupt the agglomerates in smaller ones. On the other hand, the shear thickening behaviour can be explained by means of hydro-clustering mechanism [23, 24]. As the shear rate increases the aggregates may be moved to closer positions, so, over a critical shear rate value ($\dot{\gamma}_c \leq \dot{\gamma} \leq \dot{\gamma}_m$), the aggregates may be attached

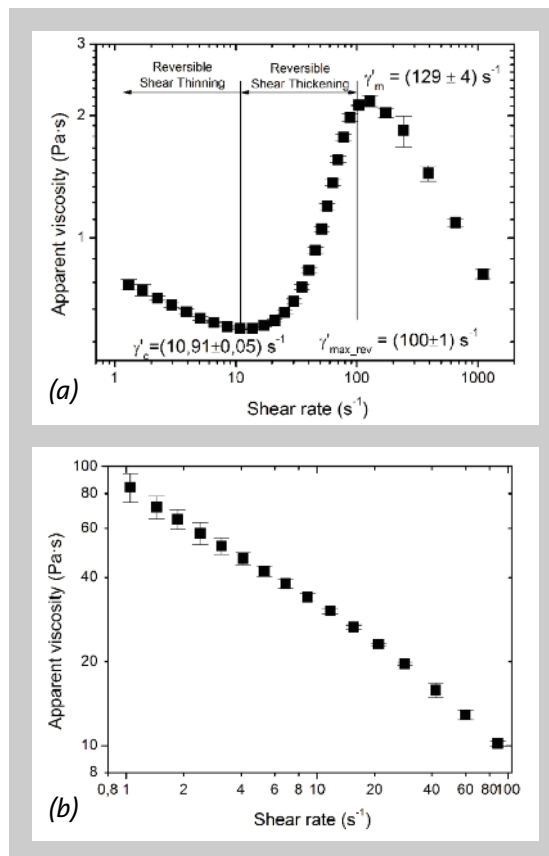


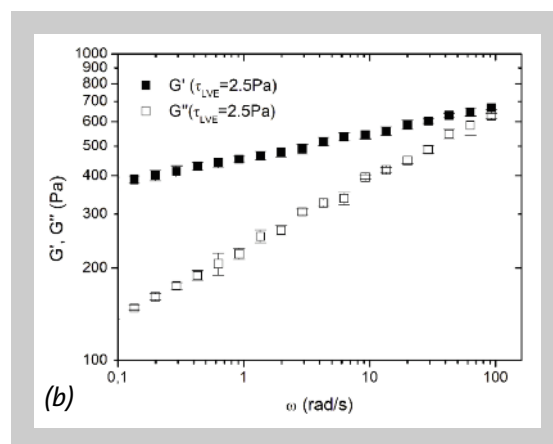
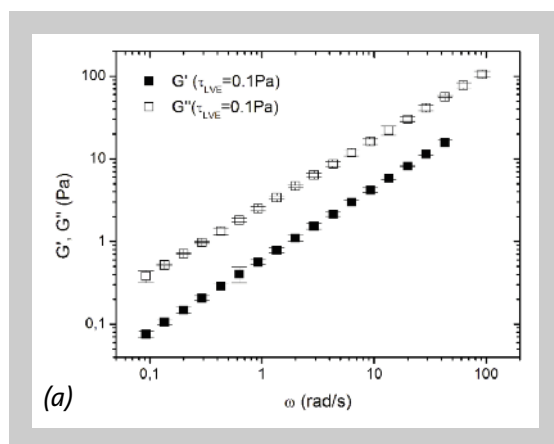
Figure 3 (left): Influence of the resting time in the transitory response of the suspensions of A200 in PPG400 and PPG2000 at 5 %v/v when undergone to a step-up in shear rate from 0 to 0.1 s^{-1} .

Figure 4: Steady state viscosity curves of A200 suspensions in PPG400 (a) and PPG2000 (b) at 5 %v/v.

each other forming bigger clusters driven by shear forces. The bigger the cluster size, the higher the resistance to flow is within them, so locally lubrication forces dominate and consequently the viscosity increase [25].

In the case of PPG2000 suspension, as the length of polymer chains is of the same order of magnitude than particle diameter (Table 1), the solvation of silica particles by PPG2000 molecules is not as effective as in the case of PPG400 suspension. Consequently, again based upon Khan and Zoeller [22], and Raghavan et al. [2] interpretations, we can assume that particle primary aggregates are able to form a volume filling network structure. The poor solvation of particles by PPG2000 molecules makes possible that a long-range order particle-particle interaction can be achieved in suspensions of A200 in PPG2000 at 5 %v/v. Therefore this system is flocculated. Besides, the formation of this network may take long time (≥ 1800 s) as was observed. The primary particle aggregates have more difficulty to move through the medium to connect each other possibly because of relative high viscosity of the suspending media. According to this explanation the proposed scheme for this material is consistent with its steady viscosity curve. The shear thinning behaviour observed in the whole shear rate region here studied is a consequence of disrupting the agglomerates in smaller ones, which is driven by the mechanical energy supplied in form of shear stress.

Figure 5: Mechanical spectra within the linear viscoelastic deformation of A200 suspensions in PPG400 (a) and PPG2000 (b) at 5 %v/v.



In spite of the fact that rheometry is a macroscopic materials characterization technique, it is well-known that provides an easily accessible way to correlate the microstructure of a system with its particular rheological responses. In line with this idea, the dynamic rheological tests are commonly used to describe states of aggregation in colloidal systems. The importance of this type of measurements arises from the fact that at low strain values the “at rest” microstructure can be probed since it is not disrupted by shearing as in steady shear flow experiments. This is very useful in colloidal systems because the state of aggregation can be associated with the particular rheological response within the linear viscoelastic regime obtained from the dynamic mechanical spectrum of the material. The typical rheological behaviour for a non-flocculated or deflocculated system is characterised by a frequency sweep within the linear viscoelastic response in which the viscous modulus dominates the rheological response ($G'(\omega) < G''(\omega)$). In opposite, the rheological response of a flocculated dispersion presents higher values for G' and G'' , due to primary particles agglomerates, and the storage modulus dominates the response ($G'(\omega) > G''(\omega)$). Because of the presence of these agglomerates, the sample exhibits a more elastic response with less marked frequency dependence for G' [9]. The limiting case, in which the forces between primary particle aggregates and the concentration allow forming a three dimensional network, G' is completely frequency independent and dominates over G'' . This type of microstructure is known as a gel and it exhibits solid-like behaviour, similar to chemically cross-linked polymeric networks [26, 27].

In order to ensure a dynamic frequency sweep test within the linear viscoelastic regime, oscillatory stress sweep tests were carried out previously. Thus, the limit of the linear viscoelastic behaviour were determined at three different frequency values (0.1, 1, 100 rad/s). Then, the limits of linear region over the frequency range 0.1–100 rad/s were established

(not shown) for both suspensions. Therefore, dynamic frequency sweep tests were done by applying oscillation amplitude within their linear region over the frequency range 0.1 - 100 rad/s. The dependence of storage modulus (G') and loss modulus (G'') with frequency were determined (Figure 5). Results confirm that the suspension of silica particles in PPG400 is non-flocculated, while in PPG2000 is weakly flocculated.

As it has been widely observed that A200 is a thixotropic agent when added to different liquid media [9, 19, 28], and as it has been observed here that A200 in PPG2000 exhibits shear thinning behaviour, we were prone to think that this suspension will exhibit thixotropic behaviour. Thixotropy implies that the viscosity will gradually decrease in time when the shear rate is suddenly increased, the time effect should be reversible and consequently the viscosity should again increase in time when the shear rate is reduced [29, 30]. Thixotropic behaviour is commonly studied by tracking the material response resulting from stepwise changes in shear rate, as the coupled effect of time and shear rate can be clearly separated in such experiments. This procedure has already been used since early studies on thixotropy, i.e. Weltman (1943) [31 – 33]. Consequently, stepwise experiments were developed in order to study time dependent behaviour of this material. The rheological test consists of three consecutive steps in control rate mode, within the reversible shear rate range ($\dot{\gamma} \leq 1 \text{ s}^{-1}$). The first step was carried out at a low shear rate, $\dot{\gamma} = 0.01 \text{ s}^{-1}$, with the objective to get an equilibrium strong structure. Once the steady state was achieved, a second step was undergone at a relatively high shear rate, $\dot{\gamma}_2 = 0.05, 0.25, 1 \text{ s}^{-1}$, resulting in a rupture of the structure, whose time evolution is measured. Finally, when the equilibrium was gained at $\dot{\gamma}_2$, the third step was applied at $\dot{\gamma}_3 = 0.01 \text{ s}^{-1}$ observing the rebuild of the structure by means of the measurement of the shear stress with time. In this way, with this experimental protocol, it is possible to analyse the time dependent behaviour of the sample during breakdown

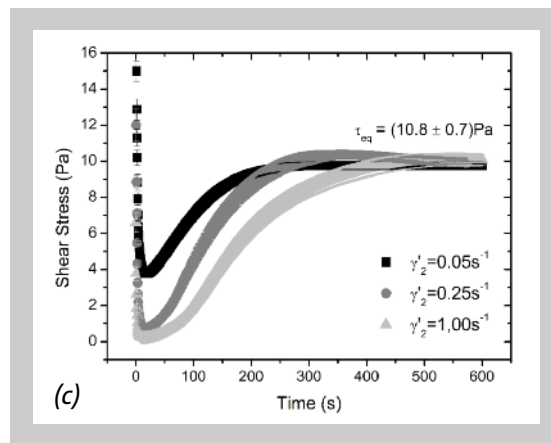
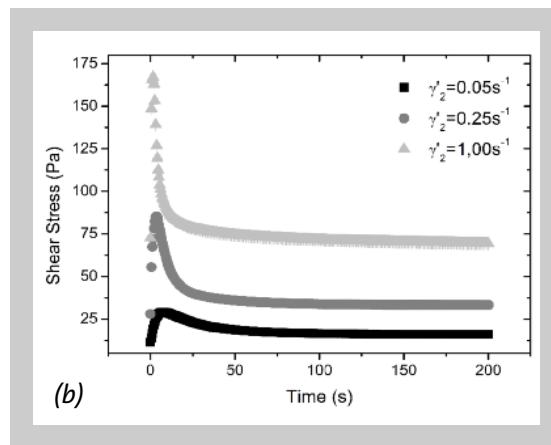
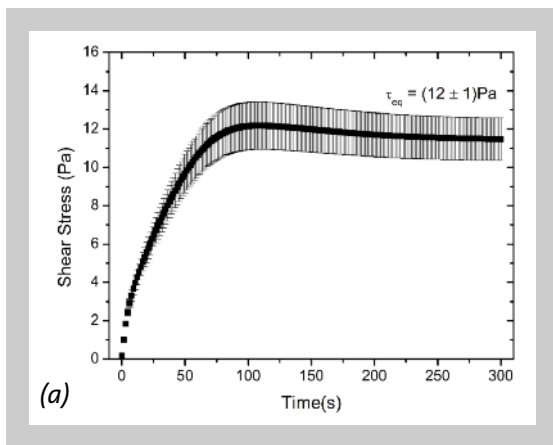


Figure 6: Transitory response of A200 suspension in PPG2000 at 5 %v/v when it is undergone to a step-up essay from 0 to 0.01 s⁻¹ (a), when it is undergone to a step-up essay from 0.01 to 0.05, 0.25, and 1 s⁻¹ (b), and when it is undergone to a step-down essay from 0.05, 0.25 and 1 s⁻¹ to 0.01 s⁻¹ (c).

and build-up transitory responses, as well as its reversibility, which is a basic condition that must be accomplished to affirm thixotropy is being observed.

Figure 6a shows a breakdown transitory response when the system is undergone to the first step from the rest. The time-dependent changes in stress and structure reveal two periods with distinct time scales in the breakdown process, situated on either side of the maximum stress and orientation of the structure, which remains connected. The second corresponds to flow and disaggregation of the structure. It has been reported by Pignon et al. (1998) [34] that the order of magnitude of the time scale in the first period is shorter than that in the second for thixotropic materials, being the ratio of the time scales of the order of 1/1000. In our case, it is clearly observed a delayed in the overshoot in $\tau(t)$ and the ratio is around 1/3. In order to study the breakdown of the microstructure, the procedure followed involves applying a jump in shear rate from an initial value ($\dot{\gamma} = 0.01 \text{ s}^{-1}$) to a final value ($\dot{\gamma}_2$) with ($\dot{\gamma}_2 > \dot{\gamma}_1$). During this test, the material passes from an aggregate structure with a certain “high” initial consistency to a less aggregated structural state, i.e. with a lower level of consistency. In Figure 6b, a delayed overshoot is observed again in the shear stress response for all values of $\dot{\gamma}_2$ here considered, but the ratios are in the order of 1/20. The overshoot can be interpreted in this case as the expression of the maximum deformation that the microstructure developed in the steady state at $\dot{\gamma}_1 = 0.01 \text{ s}^{-1}$ can support before it falls apart. After this, new softer equilibrium microstructures are formed, softer as higher is the shear rate applied to the sample in the second step-up. When the equilibrium state is reached at $\dot{\gamma}_2$, the lower shear rate $\dot{\gamma}_3 = 0.01 \text{ s}^{-1}$ is again applied to the system. As it was before pointed out, this last step-down is designed to analyse the build-up transitory response of the material (Figure 6c). It can be observed the resulting stress transients display an initial, sudden decrease that reflects the

reduction of the purely viscous stress contribution when lowering the shear rate. It is followed by a fast viscoelastic relaxation. After this, the stress monotonically increases to a steady state level as a result of the growing microstructure. Figure 6.c shows that the steady state value of the stress at the final shear rate is independent of the $\dot{\gamma}_2$ -value and the samples recover over the 90 % of the steady shear stress value which was achieved in the first step-up. This quantitative result indicates that the reversibility, a basic condition to affirm we are observing thixotropic behaviour, has been proved. This typical build-up curve has been reported before for many other for thixotropic systems by different authors [33, 34]. On the other hand, the overshoots observed starting the step tests lead us to conclude that A200 suspension in PPG2000 at 5 %v/v also presents elastic behaviour. According to Cheng [7], the combination of both time dependent behaviours can be named as thixoelectricity.

As pointed out, there are thixotropic materials in which it is possible to distinguish between the SYS and the DYS. Cheng proposed an experimental method to determine the DYS [7]. Basically it consists of applying to a thixotropic sample successive steps in shear rate and determine a family of constant structure curves and, from these, its steady-state flow curve (SSFC). The SSFC will be finally used to get the DYS. Galindo-Rosales et al. [9] have validated experimentally this

Figure 7 (left): Family of constant structure curves within the reversible shear rate range of A200 suspension in PPG2000 at 5 %v/v.

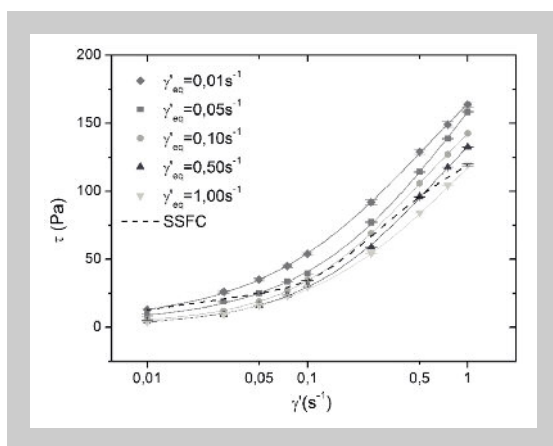
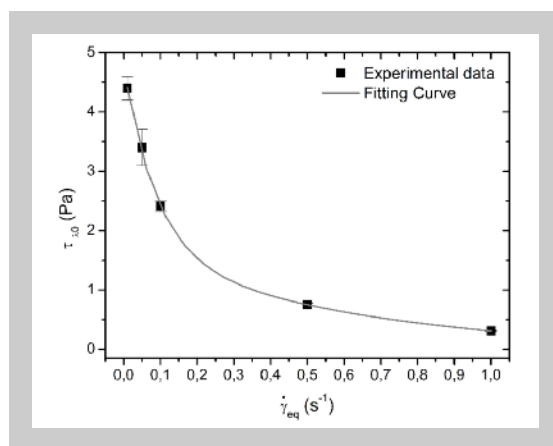


Figure 8: Representation of τ_{oy} versus $\dot{\gamma}_{eq}$ of A200 suspension in PPG2000 at 5 %v/v and fitting curve from Equation 2.



method by using aqueous suspensions of A200 at 2.5 and 7.5 %v/v. These suspensions showed thixotropic behaviour (no thixoelectric) and different values for the SYS and the DYS were obtained in both cases. Consequently, according to Cheng [7], they concluded that more than one kind of structure must exist in these aqueous systems. Following the method described, a family of constant structure curves within the reversible shear rate range of A200 suspension in PPG2000 has been obtained. Figure 7 shows the results.

Each constant structure curve represents the overshoot values of $\tau_i(t)$ with which an equilibrium structure developed in state of flux at $\dot{\gamma}_e$ responses when, suddenly, is undergone to $\dot{\gamma}_i$. It has been found that the equation which better fits each constant structure curve is:

$$\tau = \tau_{\infty\lambda} + \frac{\tau_{o\lambda} - \tau_{\infty\lambda}}{1 + (\dot{\gamma}/\dot{\gamma}_o)^p} \quad (1)$$

where $\tau_{\infty\lambda}$ and $\tau_{o\lambda}$ are interpreted as the overshoot values with which an equilibrium structure developed in state of flux at $\dot{\gamma}_e$ would response when the sample was undergone to $\dot{\gamma}_i \rightarrow \infty$ and $\dot{\gamma}_i \rightarrow 0$, respectively; p is a non-dimensional parameter and $\dot{\gamma}_o$ is a shear rate value that gives an overshoot value which is the average value of τ_{∞} and τ_o . The results corresponding to each constant structure curve are shown in Table 2. From

data shown in Table 2, a plot $\tau_{o\lambda} = \tau_{o\lambda}(\dot{\gamma}_{eq})$ has been obtained. As can be seen in Figure 8 it follows a double exponential decay equation:

$$\tau_{o\lambda} = A_o + A_1 e^{-\dot{\gamma}_{eq}/B_1} + A_2 e^{-\dot{\gamma}_{eq}/B_2} \quad (2)$$

Table 3 contains all the values of the parameters from Equation 2. According to Cheng [7], the DYS is given by the following equation:

$$\tau_d = \lim_{\dot{\gamma}_{eq} \rightarrow 0} \tau_{o\lambda} \quad (3)$$

therefore from Equation 2 the DYS is given by:

$$\tau_d = A_o + A_1 + A_2 = (4.8 \pm 0.1) Pa \quad (4)$$

The value of SYS of A200 suspension in PPG2000 was determined by applying a steady stress sweep from 0 to 100 Pa as the limit of elastic deformation range [35] (Figure 9). The result so obtained was:

$$\tau_y = (11.141 \pm 0.006) Pa \quad (5)$$

As SYS does not coincide with DYS, it can be concluded that A200 may develop at least two different kind of microstructure in PPG2000 at 5 %v/v, the robust one would be build-up under flow conditions and would be responsible for the value of DYS, while the weak one would be generated at rest. The value of SYS is consequence of the combined effect of both structures, and therefore is needed to be bigger than the value of DYS [7].

4 CONCLUSION

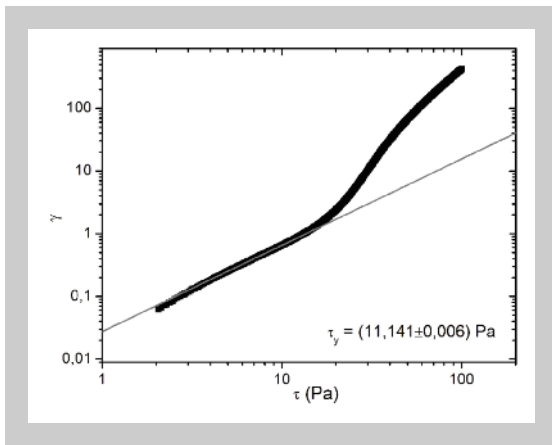
In this study we investigated the rheological behaviour of Aerosil® 200 suspensions in polypropylene glycol of two different molecular weights (400 and 2000 g/mol), and two main conclusions have been obtained. First, the length of the polymeric molecules has a great influence on the microstructure developed by A200 in PPG.

Table 2 (above): Parameter values of the Equation 1 for each constant structure curve of A200 suspension in PPG2000 at 5 %v/v. Correlation coefficient is also given for each fit.

Table 3: Parameter values of the Equation 2 applied to A200 suspension in PPG2000 at 5 %v/v. Correlation coefficient is also given.

$\dot{\gamma}_{eq}$ [s ⁻¹]	$\tau_{o\lambda}$ [Pa]	$\tau_{\infty\lambda}$ [Pa]	$\dot{\gamma}_o$ [s ⁻¹]	p	R^2
0.01	4.4±0.2	261.3±0.8	0.549±0.003	0.835±0.003	0.99987
0.05	3.4±0.3	301±2	0.91±0.01	0.876±0.006	0.99949
0.1	2.41±0.09	210.4±0.5	0.507±0.002	1.055±0.003	0.99994
0.5	0.75±0.03	222±2	0.673±0.009	0.996±0.009	0.9992
1	0.31±0.01	225±3	0.91±0.02	0.892±0.009	0.9988

A_o [Pa]	A_1 [Pa]	B_1 [s ⁻¹]	A_2 [Pa]	B_2 [s ⁻¹]	R^2
-0.061±0.001	1.726±0.002	0.65±0.01	3.111±0.003	0.088±0.002	0.999



A200 particles and PPG molecules tends to form hydrogen bonds, due to fumed silica particles are hydrophilic and the polymer is a polar organic liquid. In spite of that, it has been found that it is possible to obtain a flocculated suspension. Only it is needed a dispersing media with chains long enough, at least of the same order of magnitude that the particle diameter, to reduce the effectiveness of the solvation of the particle. Then, having resting time long enough to let the primary particle aggregates contact each other, they are able to develop a volume filling network structure. Second, the use of the experimental method proposed theoretically by Cheng [7] has been successfully applied to a thixotropic system (suspension of A200 in PPG2000 at 5 %v/v) in order to determine its DYS value. It has also been found that the value of SYS and DYS does not coincide, so more than one kind of microstructure must have been developed by A200 in PPG2000.

5 ACKNOWLEDGEMENTS

We would like to express our gratitude to Degussa A.G. for supplying kindly Aerosil®200.

REFERENCES

- [1] Raghavan SR, Hou J, Khan SA: Colloidal interactions between particles with tethered nonpolar chains dispersed in polar media: Direct correlation between dynamic rheology and interactions parameters, *Langmuir* 16 (2000) 1066-1077.
- [2] Raghavan SR, Walls HJ, Khan SA: Rheology of silica dispersions in organic liquids: New evidence of solvation forces dictated by hydrogen bonding, *Langmuir* 16 (2000) 7920-7930.
- [3] Barnes HA: The yield stress: a review or 'παντα ρει': everything flows? *J. Non-Newtonian Fluid Mech.* 81 (1999) 133-178.
- [4] Barnes HA: The 'Yield Stress Myth?' paper – 21 years on, *Appl. Rheol.* 17 (2007) 43110.
- [5] Barnes HA, Walters K: The Yield Stress Myth? *Rheol. Acta* 24 (1985) 323-6.
- [6] Moller PCF, Mewis J, Bonn D: Yield Stress and thixotropy: on the difficulty of measuring yield stress in practice, *Soft Matter* 2 (2006) 274-283.
- [7] Cheng DCH: Yield Stress: A Time-Dependent Property and How to Measure it, *Rheol. Acta* 25 (1986) 542-554.
- [8] Wallevik JE: Rheology of suspensions. Fresh Concrete, Mortar and Cement Paste, Ph.D. Thesis, University of Trondheim, Norway (2003).
- [9] Galindo-Rosales FJ, Rubio-Hernández FJ, Velázquez-Navarro JF, Gómez-Merino AI: Structural Level of Silica-Fumed Aqueous Suspensions, *J. American Ceramic Soc.* 90 (2007) 1641-1643.
- [10] Masalova I, Malkin AYA, Foudazi R: Yield stress of emulsions and suspensions as measured in steady shearing and in oscillations, *Appl. Rheol.* 18 (2009) 44790.
- [11] Degussa A.G.: Technical Bulletin - Fine Particles 18 (1989).
- [12] Degussa A.G.: Product Information (2005).
- [13] Degussa A.G.: Technical Bulletin - Fine Particles 11 (2006).
- [14] Sánchez A: Colloidal gels of fumed silica: Microstructure, surface interactions and temperature effects, Ph.D. Thesis, North Carolina State University, United States (2006).
- [15] Khan SA, Baker GL, Colson S: Composite Polymer Electrolytes Using Fumed Silica Fillers: Rheology and Ionic Conductivity, *Chem. Mater.* 6 (1994) 2359-2363.
- [16] Raghavan SR, Riley M, Fedwik PS, Khan SA: Composite Polymer Electrolytes Based on Poly(ethylene glycol) and Hydrophobic Fumed Silica: Dynamic Rheology and Microstructure, *Chem. Mater.* 10 (1998) 244-251.
- [17] Nguyen D, Jensen CTB, Kristensen PG: Experimental and modelling studies of the flow properties of maize and waxy maize starch pastes, *Chem. Eng. J.* 70 (1998) 165-171.
- [18] Jauregi-Beloqui B, Fernández-García JC, Orgilés-Barceló AC, Mahiques-Bujanda MM, Martín-Martínez JM: Rheological properties of thermoplastic polyurethane adhesive solutions containing fumed silicas of different surface areas, *Inter. J. Adhesion Adhesives* 19 (1999) 321-328.
- [19] Torró-Palau, AM, Fernández-García JC, Orgilés-Barceló MM, Martín-Martínez JM: Characterization of polyurethanes containing different silicas, *Inter. J. Adhesion Adhesives* 21 (2001) 1-9.
- [20] Raghavan SR, Khan SA: Shear-induced microstructural changes in flocculated suspensions of fumed silica, *J. Rheol.* 39 (1995) 1311-1325.
- [21] Dullaert K: Constitutive equations for thixotropic dispersions, Ph.D. thesis, Katholieke Universiteit Leuven, Belgium (2005).
- [22] Khan SA, Zoeller NJ: Dynamic rheological behaviour of flocculated fumed silica suspensions, *J. Rheol.* 37 (1993) 1225-1235.
- [23] Bender J, Wagner NJ: Reversible shear thickening in monodisperse and bidisperse colloidal dispersions, *J. Rheol.* 40 (1996) 899-916.

Figure 9: Experimental determination of SYS value as the limit of elastic deformation range of A200 suspension in PPG2000 at 5 %v/v by applying a steady stress sweep from 0 to 100Pa.

- [24] Lee YS, Wagner NJ: Dynamic properties of shear thickening colloidal suspensions, *Rheol. Acta* 42 (2003) 199-208.
- [25] Fischer C, Plummer CJG, Michaud V, Bourban PE, Manson JAE: Pre- and post-transition behavior of shear-thickening fluids in oscillating shear, *Rheol. Acta* 46 (2007) 1099-1108.
- [26] Campo L: Reometría dinámica aplicada al estudio de surimis elaborados por métodos distintos y con diversos ingredientes. Importancia de la conservación en estado congelado, Ph.D. Thesis, University of Vigo, Spain (2008).
- [27] Campo L, Tovar C: Influence of the starch content in the viscoelastic properties of surimi gels, *J. Food Eng.* 84 (2008) 140-147.
- [28] Dolz M, González F, Delegido J, Hernández MJ, Pellicer J: A Time-Dependent Expression for Thixotropic Areas. Application to Aerosil 200 Hydrogels, *J. Pharma. Sci.* 89 (2000) 790-797.
- [29] Mewis J: Thixotropy – A general review, *J. Non Newtonian Fluid Mech.* 6 (1979) 1-20.
- [30] Barnes HA: Thixotropy – A review, *J. Non Newtonian Fluid Mecha.* 70 (1997) 1-33.
- [31] Weltman R: Breakdown of thixotropic structure as a function of time, *J. Appl. Phys.* 14 (1943) 343-350.
- [32] Coussot P, Nguyen QD, Huynh HT, Bonn D: Viscosity bifurcation in thixotropic, yielding fluids, *J. Rheol.* 46 (2002) 573-589.
- [33] Dullaert K, Mewis J: Thixotropy: Build-up and breakdown curves during flow, *J. Rheol.* 49 (2005) 1213-1230.
- [34] Pignon F, Magnin A, Piau JM: Thixotropic behaviour of clay dispersions: combinations of scattering and rheometric techniques, *J. Rheol.* 42 (1998) 1349-1373.
- [35] Mezger T: *The Rheology Handbook for users of rotational and oscillatory rheometers*, Vincent Verlag, Germany (2002).

