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Correlation between large amplitude oscillatory shear (LAOS) and steady shear of soft solids at the onset of the fluid rheological behavior

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The paper is dedicated to the memory of our colleague and friend Victor Hugo Rolón-Garrido. We shall always keep alive in our memories the beautiful nights spent together in Cluj-Napoca, Romania.

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A B S T R A C T

The paper is concerned with the experimental investigations of soft solids rheology at the onset of the fluid behavior. The aim of the work is to find the correlation between the dynamics moduli measured in MAOS and LAOS oscillatory regime and the data obtained in simple shear experiments. The tested samples are represented by colloidal systems and suspensions (impression material and a cosmetic cream), both being characterized by a yield state. The present study explores the idea that yield state, determined in simple shear as the onset of the plateau in flow curve, corresponds to the MAOS region and the yield point coincides with the location where the viscous modulus discloses a relatively peak against the strain amplitude. It is proved experimentally that flow onset, up to now manly determined in simple shear, is also detectable using the oscillatory strain amplitude sweep test and corroborated by the FT-rheology analysis of the data. So, the yield point is more precisely characterized by a critical value of strain, rather than a unique value of the yield stress. Since the yield state is one of the main rheological characteristic of soft solids/matter rheology, it is of major interest to have at hand a procedure for characterization the onset of material fluid behavior and to detect possible presence of wall depletion phenomena.

The results of this study demonstrate that for materials in which the yield state is present qualitative and quantitative relations between the data from simple shear and oscillatory tests can be established.
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1. Introduction

The rheology of soft solids (sometimes called as structured liquids, [1]), as entangled polymers [2], polymer glasses [3], dense suspensions [4,5] (as polymers solutions mixed with particles), soft entangled materials (e.g. wormlike micellar solutions) [6–8], lubricated greases [9,10], metastable colloidal systems (e.g. gels) [11–14], and soft particle glasses [15], classifies these materials as complex fluids characterized by a concentrated phase (e.g. polymers, solid or soft particles) dispersed in a homogeneous liquid (solvent). These materials might also be considered as yield stress fluids, since they normally develop during simple shear, or periodic flow, shear induced micro-structural changes leading to a transition between solid-like and fluid-like rheological behavior [1].

Transition from solid to fluid, or inversely (as sol-gel transition [16]), is known as yielding process. The shear stress associated with the onset of fluid behavior is called yield stress (σ_0); when shear stress exceeds this critical value the material starts to flow with a strong shear thinning character of the viscosity function.

Scientific literature provides multiple definitions of yielding behavior, all related to the time scales involved in the flow: relaxation time of the material, experimental time scale, the time in which the components are reacting chemically one to another forming networks (cross-linking, branching) which induce changing of the material's internal structure. For materials which contain hard solids (glasses, wax particles, powders) [5,13], or soft solid particles [11,15,17,18] the yielding behavior is related to the kinematics of deformation; Brownian motions and volume extrusion might be also the cause for yielding in some suspensions and colloids.

Generally the yielding mechanism is considered to be produced by the presence of a weak elastic network which is broken within the base fluid under applied deformations; beyond the yield state (characterized by a yield stress or yield strain) the material behaves

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as a fluid. At low applied deformations, the accumulated internal tension makes the network structure to respond elastically, in many cases similar to a soft solid with a linear dependence between applied deformation and stress. The material is not relaxing under low applied stresses, but the internal network structure changes continuously in time; when reaching the yield state it relaxes leading to a fluid behavior. Almost all soft solids in vicinity of yielding disclose an unstable rheological state where elastic and liquid phases coexist. Of particular interest is the transition domain between solid-like and fluid-like behavior where the shear induced micro-structural changes manifested at macroscopic scale through unexpected non-linear distribution of the measured rheological properties (flow curve, viscosity, dynamic moduli), or spurious phenomena like wall slip, wall depletion [19–21], or shear banding [2,7,21–28].

In the vicinity of transition the materials might exhibit in simple un-steady shear regime and in dynamic tests local thickening of rheological properties (viscosity, loss modulus), phenomena associated to a yield point: a well-defined value for the stress or strain within the yield state, in the limit of steady state [9,10,22,26,29,30] (which normally requires a very long experimental time to be achieved).

In the vicinity of yield point, the non-monotonic behavior material functions are emphasized by both simple shear and dynamic rheological measurements. In the case of simple shear flow a plateau region of the flow curve and a clear demarcation between different flow regimes is observed (in both control stress and control strain modes) by stress/strain sweeps or multiple creep/relaxation tests.

This class of materials discloses during the dynamics of simple shear flow a rheological response which follows a particular pattern highlighted by a transient non-monotonous flow curve. In the limit of steady shear, the flow curve discloses an instability zone called "jump" or "plateau", where sharp change in shear rate is measured at almost constant shear stress. Such a flow curve allows the delimitation between the linear viscoelastic behavior (small shear rate values, almost constant viscosity), the non-linear viscous behavior (large shear rates, shear thinning viscosity) and an unstable transition zone between them. The "jump" occurs for a certain domain of stress (or strain) values, depending if the material reaches the yield state. Within the yield state, the onset of plateau defines the yield point which depends also on the experimental initial conditions [31–34], (especially the initial state of the normal stresses). When an abrupt increase in deformation at constant stress occurs, the fluid behavior usually changes into a power-law dependence of steady shear stress on steady shear rate, with a significant lower exponent than before yielding [1,7,12,17,35,36].

The rheology of complex fluids is commonly probed through dynamical oscillatory shear measurements. In the linear regime, at a perfectly sinusoidal strain input signal the material response in stress $\sigma = \sum_{k=1}^{n} \sigma_k \cdot sin(k\omega t + \delta_k)$, is a simple harmonic function ($\sigma_k \equiv 0$ for $k \geq 2$) oscillating with the fundamental frequency dictated by the applied strain, $\gamma = \gamma_0 \cdot sin\omega t$, with a phase angle dependent only on the applied angular frequency, $\delta = \delta(\omega)$. When the amplitude of the input signal is beyond a critical value, the stress response deforms from a perfectly sine function and higher odd harmonics are needed for reconstruction of the output signal. Depending on the input amplitude and frequency values one can make delimitation between the existences of two characteristic flow regimes: a linear domain for small amplitudes of oscillatory shear input (SAOS) and a non-linear regime for large amplitude oscillatory shear flows (LAOS) [4,6,37], with a transition domain (MAOS) between these two regimes [38]. Therefore, the qualitative and quantitative analysis of the output stress is based on the signal decomposition using FT-rheology [4,6,17,39–42], or Chebyshev polynomials, [35,43,44]. The LAOS techniques generate not only value data to have a better characterization of the material's rheology within the non-linear regime, but also offer a better insight of the yielding process in complex fluids (as soft colloids [30] or concentrated soft and hard-sphere suspensions [45]).

One aim of the present work is to explore the idea that yield state determined in simple shear corresponds to the MAOS region and the yield point coincides with the location where the viscous modulus discloses a relatively peak against the strain amplitude. Non-monotonic behavior of dynamic functions (in particular the loss modulusG'') is observed mainly in MAOS region, which we believe corresponds in the simple shear flow to the "jump" or "plateau" in flow curve. We have to mention that some concentrate suspensions disclose in shear flow multiple plateaus previously to the onset of the flow, normally associated to the onset of LAOS region, [5].

The interest for this rheological behavior comes from the necessity of a better understanding of soft solids dynamics under medium and large deformations, which are common to many applications during production, processing and use of these materials [6,35].

A general classification of the complex fluids can be made regarding the variation of their elastic and viscous components in the nonlinear domain. Four types of rheological behaviors have been indicated until now in literature [35,46]: (i) strain thinning (type 1), (ii) strain hardening (type 2), (iii) weak strain overshoot (type 3) and (iv) strong strain overshoot (type 4). For the first two classes the elastic modulus G' and viscous modulus G'' decrease, and respectively increase, with strain amplitude. Of interest are materials which belong to the third and fourth class, where a maximum is observed in the distribution of G'', and sometimes G', when they are passing through the medium strain amplitude domain, before decreasing at large strain amplitudes. The third type is characterized by an important viscous contribution in the MAOS domain and a maximum appears only for G'' [33,35,38,47]. Suspensions, pastes, dispersions, concentrated emulsions, polymer solutions and soft glassy materials are part of this class of materials. Depending on the nature of the investigated sample this rheological behavior is explained in several ways in literature. The peak in G'' distribution has been associated with changes in materials micro-structure, the destruction and reformation of material's internal network junctions [6,38]. For entangled systems the maximum in loss modulus is generated by the entanglement and disentanglement of the branches [8,35,48]. Some explications of this phenomena are also related to an instantaneous increase of the effective volume of materials network structure, increasing of the flock size (associative polymers), to cluster formation and rearrangement during shear or generated by glass transition [6,17,35,38,40].

The fourth class of materials is characterized by an almost equal contribution of the elastic and viscous components that exhibit a maximum during MAOS, which occurs in the vicinity of the crossing point between components, as was observed for associative polymer solutions [35,38,46]. Sometimes the loss modulus variation against oscillatory strain amplitude [37,49], frequency [8,46,49] or shear stress amplitude [11], exhibits two maximum. This behavior has been recorded for a variety of materials like: comb homopolymer melts of polystyrene with entangled branch chains [38], reverse worm-like micelles composed of lecithin and urea [8], biopolymer solutions [50], suspensions containing anisotropic shaped particles [5], hard-sphere suspensions [49], peanut butter [37]. For entangled polymers the phenomena is associated to the entanglement and disentanglement of the branches depending on the applied frequency: one peak is assigned to the disentanglement (high frequencies) and the second one to backbone

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relaxation (low frequencies) [38]. In the case of suspensions containing hard spheres the observed peak might be related with constrains imposed to the material structure by the entropy increasing in the system [5].

For MAOS and LAOS domains dynamic moduli are increasing proportionally with the applied frequency, same for the size of the peak in G'' (and$G\prime$, if it is the case) [17]. In concentrated suspensions the occurrence of this non-monotonous variation of the dynamic moduli is also dependent on the shape of particles and volume fraction. The peak in G'' was observed to be larger for high volume fractions and sometimes two maxima are found in its distribution at intermediate volume fractions [5].

Non-monotonous flow curve, "plateau" region measured in simple shear tests and un-usual "peaks" in the distribution of elastic and viscous (mainly) dynamic moduli are related to micro-structural modifications, which in some conditions generate macroscopically phenomena like shear banding and apparent wall slip, [23,24,26,28,51].

It is important to mention that SAOS tests for complex fluids with yield stress are correlated with steady shear flows, as it has been proven by various studies based on experimental or numerical investigations [52–54].

Despite the published works in the last decade, still a clear testing procedure and rheological characterization in MAOS and LAOS domains remains an open subject for fluids with yield stress [30,43,55]. In this context, the authors consider that the present experimental work on the rheology soft solids/matter is welcomed for scientists with interest in the rheometry of yield stress fluids.

The goal of our paper is to investigate the non-monotonicity of materials functions measured in the yield region and to correlate the results obtained in simple shear and dynamic tests. At the end, an experimental procedure to determine the yield point within tested samples is proposed, based on the FT-rheology analysis of the oscillatory test in the MAOS region.

2. Materials and methods

2.1. Materials

The samples under investigations are: (i) polysiloxane - PS and (ii) a commercial cosmetic cream (CR). Lanolin and glycerin have been also tested as reference samples for a typical soft solid rheology (lanolin), respectively for a dominant viscous Newtonian behavior (glycerin).

The PS-sample is a condensation-curing addition silicone with low consistency used in dental applications (ISO 4823). Corresponding to standard description the sample is a light body material with low consistency and viscosity, containing polydimethylsiloxne, organic peroxide and surfactants.

Cosmetic cream is a mixture of various solvents (water, glycerin, oils), emulsifiers, preservatives solutions (Imidazolidinyl Urea, Propylparaben, Methylparaben), surfactants (Cetyl Alcohol, Ceteareth-20), and solid particles (pigments, CI 47005, CI 14700, antistatic ingredients). Surfactant components of our sample (especially urea) can form in combination with water and oil different molecular assemblies (micelles, liquid crystals). Considering the complexity of sample's structural network, the occurrence of non-linearity is expected during experimental investigations in both simple shear and dynamic testing modes.

Lanolin sample is a waxy raw material with a complex microstructure, predominantly composed of long chain waxy esters, considered generally as emulsion, with a similar rheological behavior as lubricating greases.

2.2. Experimental methods

The measurements were carried out with a commercial Physica Anton Phaar MCR 301 rheometer using plate-plate (25 mm diameter, nominal gap of 0.3 mm) and cone-plate (50 mm diameter, angle of 1°); the upper tool is rotated and the lower is at rest, the measurements of torque and angular rotation angle being performed at the upper tool. Measurements were performed at constant temperature of 20° C in both controlled strain and controlled stress mode.

Shear stress sweep tests were used to determine transient flow curves for the cream sample. Multiple creep, stressing and stress relaxation tests were carried out for the PS sample in order to build a steady state flow curve for this material. Elastic and viscous components were determined for all analyzed samples through multiple dynamic amplitude sweep tests performed at different frequency values.

No rough surfaces or special techniques were used to avoid a possible slip of samples during the experiments. After the squeezing of the samples to the experimental gap, it was always waiting before to start the shear test for the relaxing of the induced normal stresses. Each test presented and discussed in this paper was performed under same conditions at least two times with almost identically results.

3. Results and discussions

The investigations started with multiple dynamic strain amplitude sweep tests performed for all of our samples at different angular frequencies, $\omega\in[1\div50\ rad/s]$. Fig. 1 shows the materials elastic ($G\prime$) and viscous (G'') moduli obtained at $\omega=1\ rad/s$. A purely viscous response is found for the glycerin, its elastic component being absent. The lanolin sample has a solid-like behavior ($G\prime>G''$) for small strain amplitudes and a liquid-like behavior ($G\prime<G''$) after the crossing point at very low strain amplitude ($\gamma_0\cong0.03$). However, the high values of both moduli is a typical rheological behavior of soft solids (type 2) [35,47], in comparison with the non-monotonous distribution of $G\prime$ and G'' observed in the case of cream (CR) and polysiloxane (PS), samples considered soft matter materials.

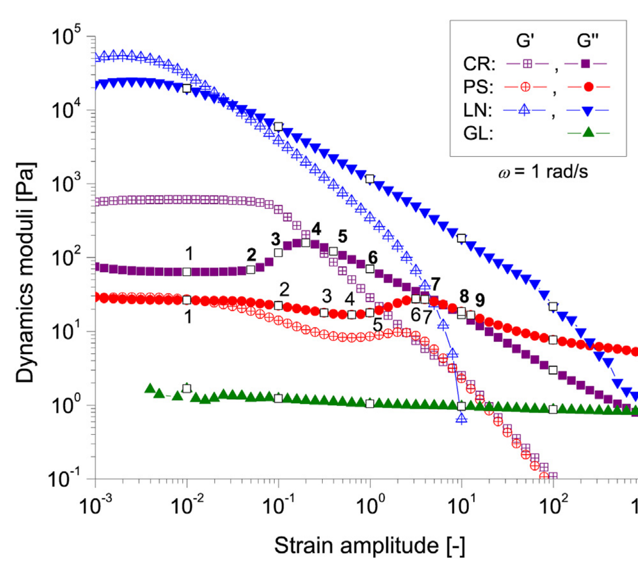

Fig. 1. Dynamic strain sweeps at constant angular frequency: cosmetic cream (CR), polysiloxane (PS), lanolin (LN) and glycerin (GL). Hollow marks indicate the points where the Lissajous figures were extracted.

An unusual increase of the viscous modulus is found for CR sample in the vicinity of the crossing point ($\gamma_0 \cong 0.25$). The relatively maximum (called also "peak") appears at a strain value of $\gamma_0 \cong 0.2$ which indicates a non-monotonous rheological behavior, classified in literature as a weak strain overshoot behavior (type 3) [35,47].

In the case of PS sample, both $G\prime$ and G'' disclose a peak. It is easily observed that PS sample has a pronounced viscous behavior in comparison with CR sample ($G\prime \leq G''$) for almost the whole tested strain amplitudes. At a critical strain of $\gamma_0 \cong 0.012$ the elastic modulus starts to decrease and the sample behavior changes from a weak elastic behavior ($G\prime$ and G'' have almost same value) to a liquid dominated one. However, this transition seems to be unstable since for both viscous and elastic components are recorded fluctuations before the onset of fluid behavior (where both moduli begin to decrease monotonically). The relative peak is present for $G\prime$ at a strain of $\gamma_0 \cong 2.50$, followed by an abrupt decreasing. In the case of G'' the peak occurs at a strain value of $\gamma_0 \cong 3.15$ and its decreasing is lower than$G\prime$ at higher strain amplitudes. This type of behavior is less met in literature being specific to associative polymers; it is classified as a strong strain overshoot behavior (type 4) [35,47].

The numbers shown in Fig. 1 indicate the points on G'' curve selected for a further more complex analyze in terms of the Lissajous figures, in order to obtain a better understanding and characterization of this complex rheological behavior associated to the yielding. Applying a sinusoidal deformation (input) to a sample, material's stress response (output) is expected to have also sine waveform, at least at small applied deformations.

In Fig. 2 are presented for CR sample the distributions of the shear stress and dynamic moduli against strain amplitude for frequencies in the range of $\omega \in [1 \div 30\ rad/s]$. Here the delimitation of the three oscillatory regimes is easily observed, being independent on the frequency value. Therefore, a linear regime is observed at small amplitude oscillatory shear strain values (SAOS) $\gamma_0 < 0.05$; a medium amplitude oscillatory shear (MAOS) for $0.05 < \gamma_0 < 5$ (where the transition from solid-like to liquid-like behavior is made and the instability in material structure is pronounced) and a large amplitude oscillatory shear domain (LAOS) for $\gamma_0 > 5$.

In the case of CR sample the frequency dependence is manifested only in MAOS and LAOS zones, in SAOS the stress amplitude being a linear function of the strain amplitude $\sigma_0 = \sigma_0(\gamma_0)$. This behavior is typical for gel-like material structures and the shape of the signal places our CR sample somewhere between soft and hard gel behavior (see also Fig. 8) [35]. When entering MAOS region shear stress amplitude starts to manifest a dependency on the applied frequency $\sigma_0 = \sigma_0(\gamma_0, \omega)$, Fig. 2a, which is amplified approaching the LAOS domain. This behavior is well emphasized by the loss modulus distribution, which discloses in MAOS region a remarkable peak at the value of strain amplitude in the range of $\gamma_0 \in (0.2 \div 0.3)$ for all applied frequencies. Furthermore, the G'' values found in the SAOS regime and the maximum value reached in MAOS region increases with oscillatory frequency, this dependence being well marked for $\gamma_0 > 5$, where the onset of LAOS regime is considered, Fig. 2c.

In Fig. 3 are shown the flow curves of CR sample obtained through multiple stress-controlled tests at imposed shear stress that increases (filed points) or decreases (open points), in the range $\sigma\ \varepsilon\ [1 \div 400]\ Pa$, with different slopes in time. The flow curves exhibits a "plateau" zone for shear rates $\dot{\gamma} \in (0.002 \div 2)\ s^{-1}$ and $\sigma \in [30 \div 110\ Pa]$, depending of the history of the imposed load, respectively deformation. We have to notice that limit stress values of this instability/jump zone delimits also the MAOS domain at low frequencies, σ_{01} and σ_{02} in Fig. 2a. At $\sigma_1 \cong 210\ Pa$ shear stress distribution tends to form a second (smaller) plateau before entering the LAOS region and changing its slope from almost Newtonian one, previous to the jump, to a strong shear thinning behavior. The sample discloses at very small shear rates a well-defined zero shear viscosity. The observed jump in shear rate under a constant applied shear stress is associated either with intrinsic instability of the constitutive relation [31], or to the slip of the sample at one plate. In the first case we can speak about a real yield stress which determine a "kink" in the velocity distribution within the gap, keeping valid the adherence conditions at the walls, [14,26,29,31,53].

This definition of yield stress associates its value with the corresponding shear stress of the jump. Although the jump has not a very precise location on the flow curve $\sigma(\dot{\gamma})$, one can observe that critical point of the plateau onset is well defined by an unique strain value γ_{cr}, Fig. 4a–b respectively $\gamma_{cr} = 0.28$, which corresponds to the interval where the peak in G'' is observed, Fig. 3c.

In comparison to CR material, the PS sample responds similar to a viscoelastic material, with a shear stress amplitude increasing directly with both strain amplitude and frequency $\sigma_0 = \sigma_0(\gamma_0, \omega)$, Fig. 5a.

In the MAOS region, $\gamma_0 \in (0.03 \div 20)$, stress response fluctuates, the moduli decreasing and increasing with strain amplitude, passing through a relatively peak before to enter the LAOS domain, Fig. 5b–c. The presence of this instability and the peaks in $G\prime$ and G'' are more relevant at low values of angular frequency ($\omega \leq 10\ rad/s$), the phenomena being diminished with increasing frequency.

Both moduli decrease once entering the unstable zone until they reach a critical strain amplitude ($\gamma_0 \cong 0.5$) and start to increase. The peaks (G'' peaks appearing earlier than for $G\prime$) are present at strain amplitude of $\gamma_0 \in (2.3 \div 3)$, shifted to lower values in this range by increasing frequency.

Multiple creep, stressing and relaxation tests were performed for the PS sample in order to determine a quasi-steady flow curve, Fig. 6. Under different values of the applied shear stress the dynamics of the samples disclose around the value $\sigma \cong 50\ Pa$ a plateau behavior in the flow curve. A shear stress domain of $\sigma \in [40 \div 60]\ Pa$ is established for $\dot{\gamma} \in (10^{-4} \div 10^{0})\ [1/s]$, where the material presents a less predictable behavior, zone which corresponds to the MAOS region in the oscillatory test.

The shear and oscillatory tests of the PS sample are connected (similar as for the CS sample) by a critical strain value $\gamma_{cr} \cong 3$ [-] which is found in creep, Fig. 7, and in the location of the G'' peak, Fig. 5c.

However, the two tested samples disclose a different behavior in frequency sweep experiment performed in SAOS regime, Fig. 8. Within the small amplitude domain CR exhibit a gel-like behavior with $G\prime$ and G'' almost parallel and the PS sample has a shear-thinning viscoelastic behavior, passing form solid-like ($G\prime > G''$) to liquid-like ($G\prime < G''$) behavior at a frequency value almost equal to unit.

The Lissajous figures are representations of raw stress response vs. strain (or shear rate) for the whole period of oscillation. For viscoelastic materials in the non-linear regime (MAOS, LAOS) the shape of Lissajous loop deforms from its original ellipsoidal shape due to the deformation of the stress output signal. Therefore, it is expected that the shape and area of Lissajous figures contain value information on the change in the material rheology with the increasing of the input magnitude. Fig. 9 show the Lissajous loops for CR and PS samples at a constant frequency $\omega = 1\ rad/s$, corresponding to the points indicated in Fig. 1.

When strain increases at the end of SAOS domain the viscoelastic behavior of CR sample, showed by the ellipsoidal shape of the loop (P1), starts to change. The area of loop increases with strain amplitude and its shape deforms, stretches horizontally and flattens vertically tending to a square-like shape at high strains. The

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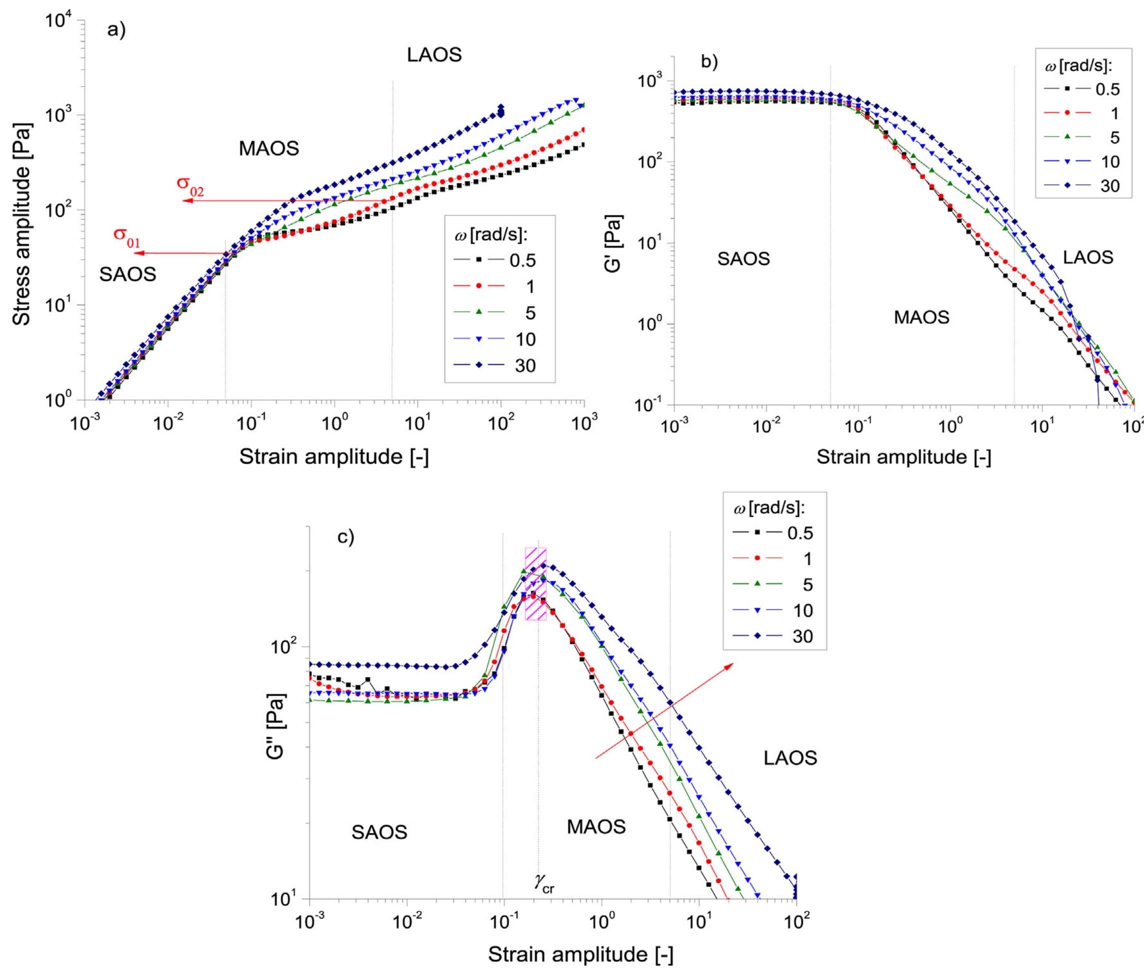

Fig. 2. Dynamic strain sweeps at various angular frequency values for CR sample; delimitation of the flow regimes for the stress amplitude (a), elastic modulus (b) and viscous modulus (c) as function of the input strain amplitude.

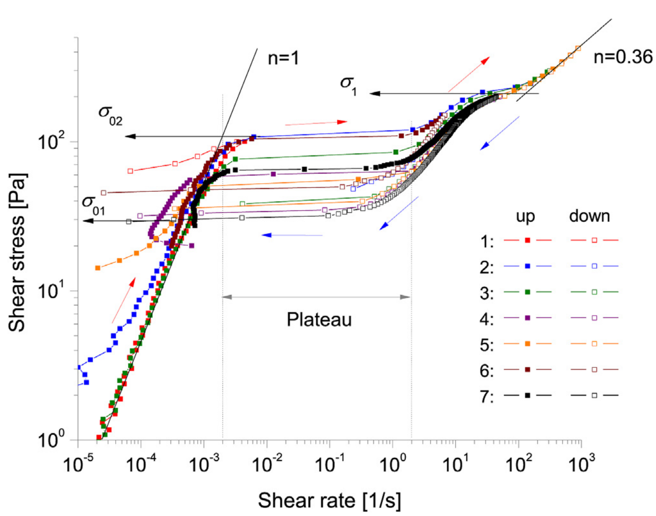

Fig. 3. Transient up/down flow curves (shear stress *vs*. shear rate) for CR sample (stress controlled experiments [54]), see Fig. 2a for the correspondence of the shear stress values σ_{01} and σ_{02}.

clockwise rotation of the loops indicates a gradual softening of the material with increasing strain amplitude, [44]. The elongated distorted shape of the curves disclose a weak strain-stiffening behavior and as approaching larger strains (in LAOS region) the rectangular shape indicates a shear-thinning behavior and a gel-like structure of our sample [35,44].

In the case of PS sample, as entering the MAOS region the Lissajous figures deform with the similar evolution as for the cream sample. The shape elongates horizontally and flattens vertically (P4, P5) but then it rotates counter-clockwise and takes almost an oval shape (P6, P7) tending to a circle shape in LAOS region (P8, P9). PS sample discloses also a weak strain-stiffening behavior with increasing strain amplitude but unlike CR sample, PS has a more pronounced viscous character in MAOS and LAOS zones. The differences between the structure and evolution of the two tested soft matters are evidenced in Fig. 10, where the normalized Lissajous loops are plotted for the peak points of viscous modulus G'', Fig. 1. The cream sample tends to a strain stiffening gel behavior, the elongation of the loop showing also a weak strain overshoot, given only by the viscous component. In the case of the PS sample the loop tends to an oval shape, stretching and widening in the same time because of the contribution of both viscous and elastic components.

The area of stress/strain Lissajous figure is proportional with the viscous energy dissipated by the system [6,35,43], whereas the area of stress/strain rate shows the energy stored by the material structure [55]. Looking at the evolution of Lissajous loops areas from Fig. 11a–b, first notice a monotonic increasing in the case of GL and LN samples, as expected since they disclose a simple and

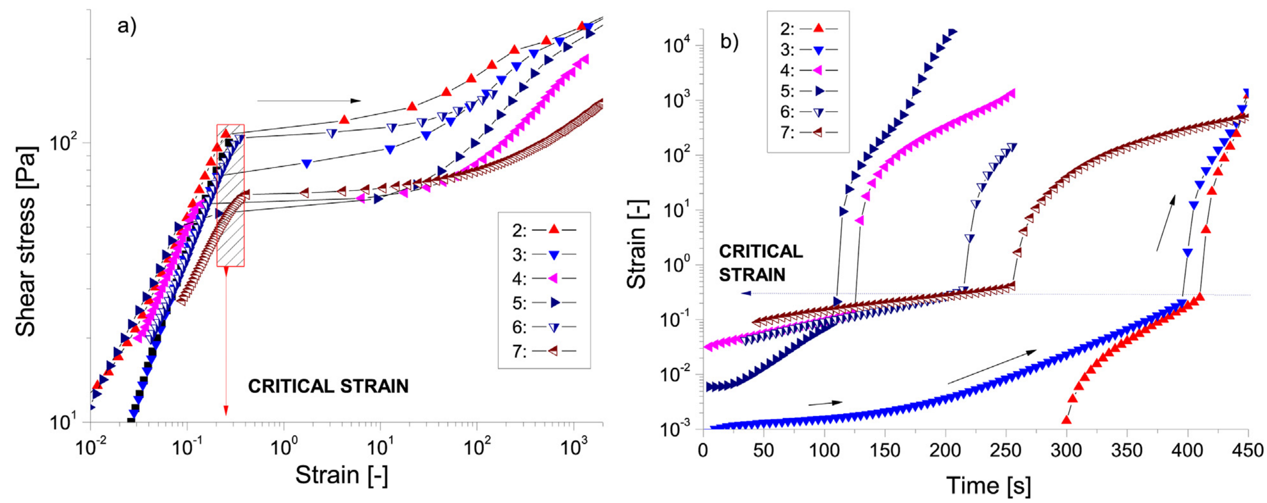

Fig. 4. Critical strain value emphasized for CR sample in shear experiments from Fig. 3: a) applied shear stress *vs.* strain, b) strain *vs.* time.

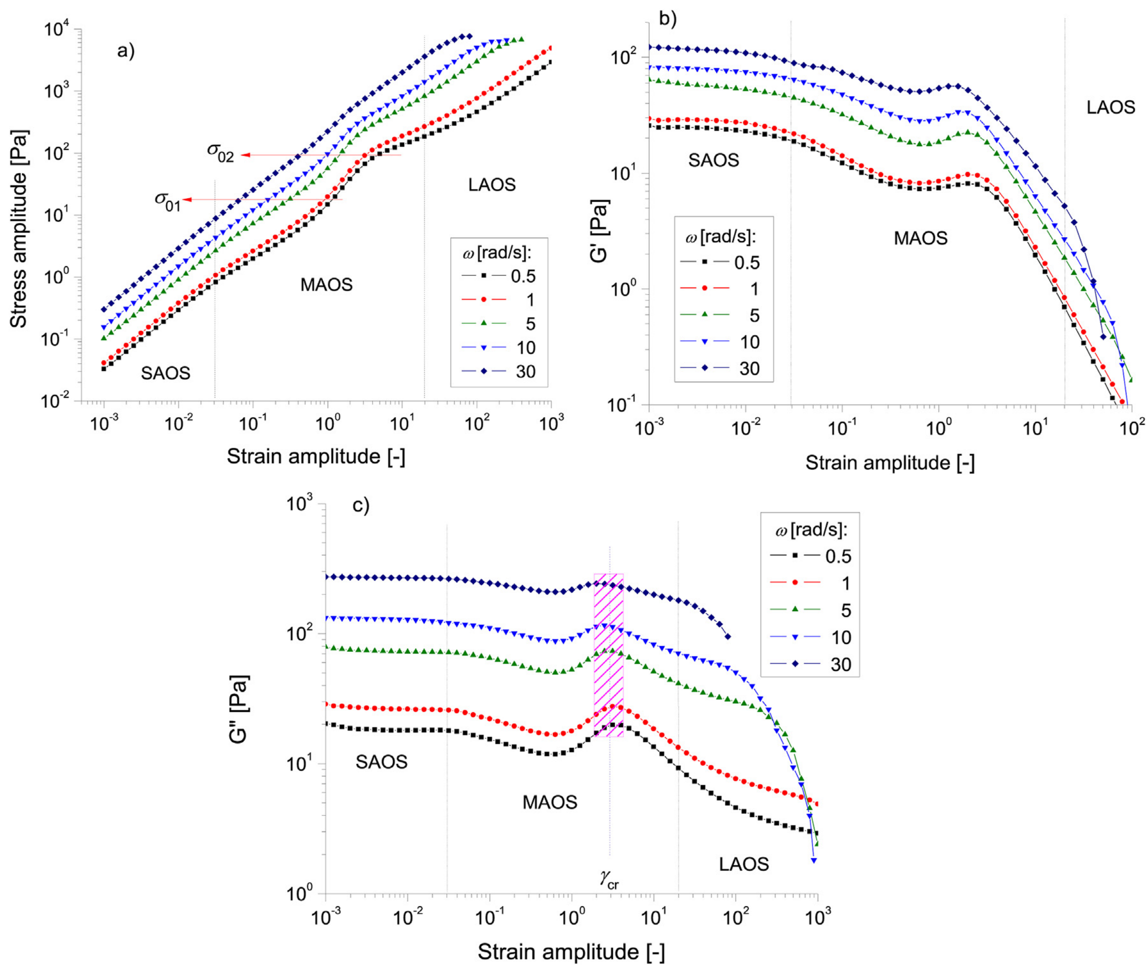

Fig. 5. Dynamic strain sweeps at various angular frequency values for PS sample; delimitation of the flow regimes for the stress amplitude (a), elastic modulus (b) and viscous modulus (c), as function of the input strain amplitude.

predictable rheological behavior, Fig. 1.

In the case of CR sample the area of stress vs. strain loop increases at different rate once entering MAOS region (corresponding to the peak in G''), meaning the viscous energy is dissipated probably due to the breakup of the network microstructures that had already stored tension at the beginning of the flow, as indicated by the increase of stress vs. strain rate curve area. In the case of PS sample, same phenomena as for CR sample is observed in stress vs.

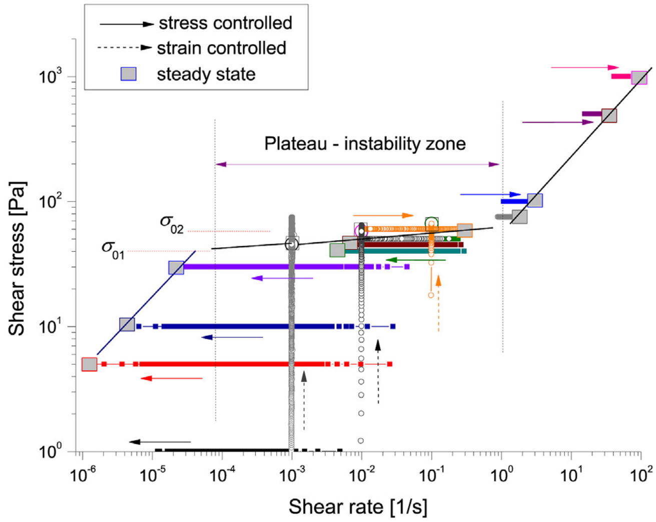

Fig. 6. Quasi-steady flow curve for PS sample (multiple stress and strain controlled shear tests), see Fig. 5a for the correspondence of the shear stresses values σ_{01} and σ_{02}.

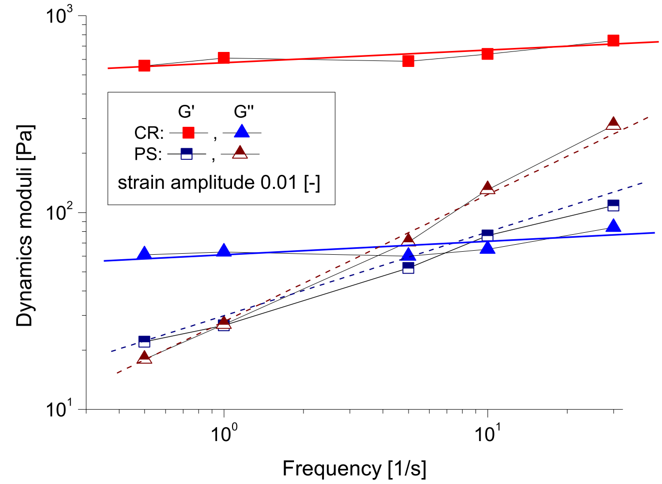

Fig. 8. Dynamics moduli *vs.* angular frequency in SAOS regime for CR and PS samples: gel structure for CR, respectively transition region for PS.

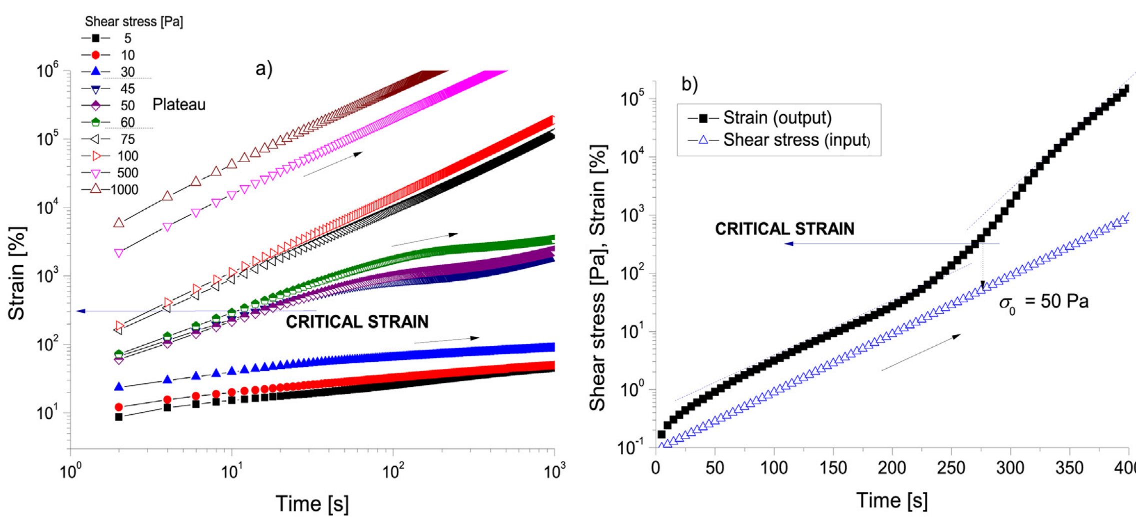

Fig. 7. Creep curves performed for the PS sample: a) constant shear stress, see Fig. 6; b) shear stress sweep. In both experiments is emphasis the same value of critical strain, i.e. $\gamma_{cr} \cong 3$ [-], which corresponds to the plateau onset in Fig. 6.

strain loop. During the transition zone, the dissipated energy in PS sample seems to be increasing with a smaller rate than the stored one, indicating a strong strain overshoot in MAOS region (accumulating tension in the structure) and a strain thinning at large strains where the system dissipates more energy but it stops accumulating (from the decrease of area stress vs. rate). As is expected, for both samples the maximum of the rate areas increasing is reached at the critical values of the strains already found in the previous experiments.

One conclusion is that tested soft matter samples discloses in a shear flow a critical strain value, γ_{cr}, which define the onset of the liquid-like behavior. This value is associated to the existence of a plateau in flow curve and to the relatively maximum of viscous modulus in strain amplitude sweep experiment. The plateau might be also related to the jump in strain rate at a constant value of shear stress, σ_0. In this case, the yield state is given by the pair (σ_0, γ_{cr}), the strain value γ_{cr} being the characteristic measure of the critical yield point.

Since the plateau in flow curve is directly related to a jump in shear rate, it is important to make difference between the existence of the yield state and possible slip at the boundary. Some "wall depletion phenomena" might generate in shear flows similar experimental findings and the distinguish between them is not trivial in the absence of an ultra-high resolution visualization system, at which our laboratory has not access at this moment. As we already mentioned, the present experimental findings are considered related to the intrinsic/bulk material rheology and not with the boundary effects, since we found a perfect correlation between the data in shear and in oscillations tests.

The rheometry performed in the non-linear domain (MAOS and LAOS regimes), corroborated with sets of strain and stress controlled shear experiments, might be a solution to find a proper answer to this intrigue "rheological question": is the deformation process of the samples characterized by a yield state, or the material is subject to slip at the boundary ?

However, the experiments prove that observed macroscopic phenomena is characterized by the same value of the strain, which make sense if that critical strain value is a well-defined material

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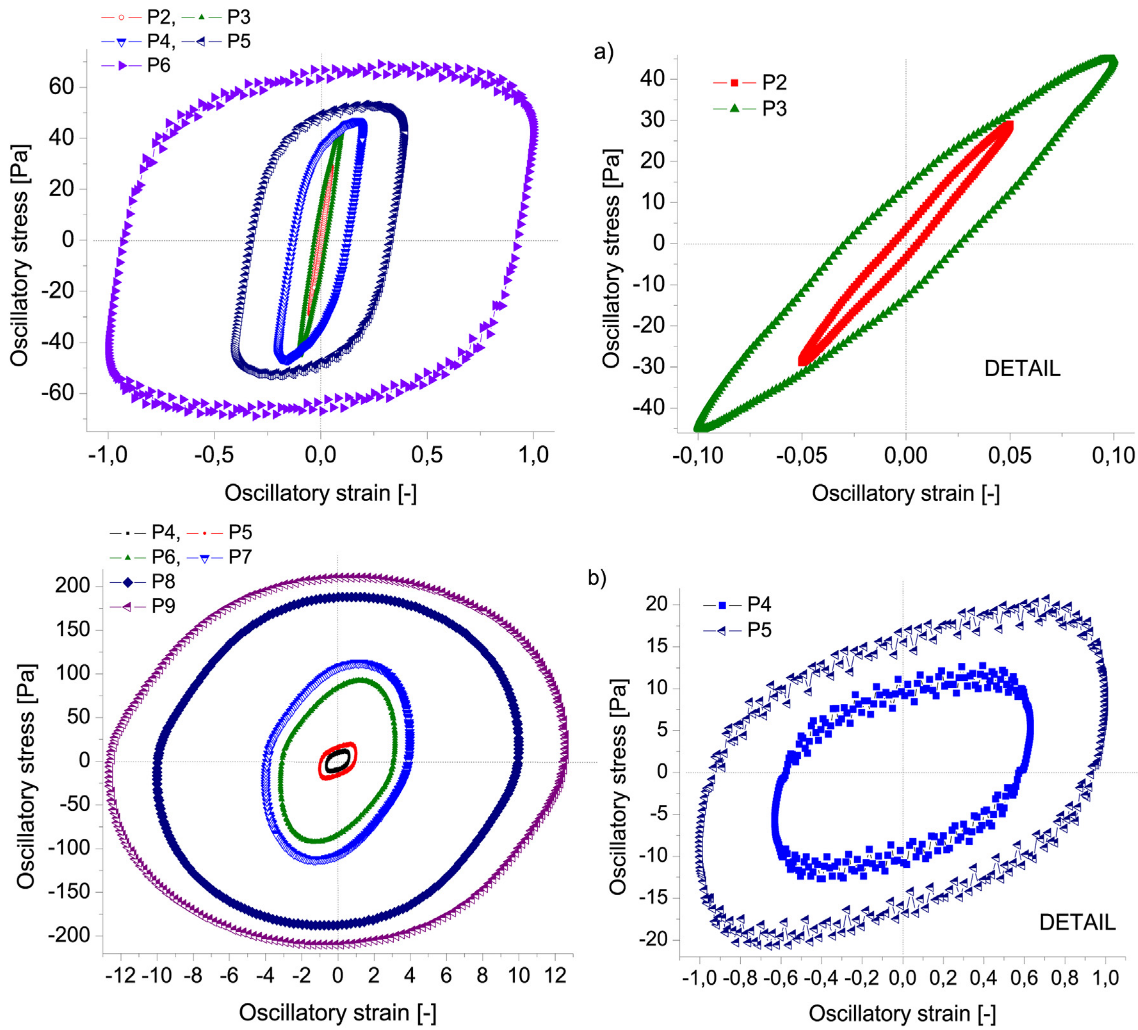

Fig. 9. Lissajous figures, oscillatory stress *vs.* oscillatory strain, for CR sample (a) and PS sample (b) correspond to the points indicated in Fig. 1 ($\omega = 1$ rad/s).

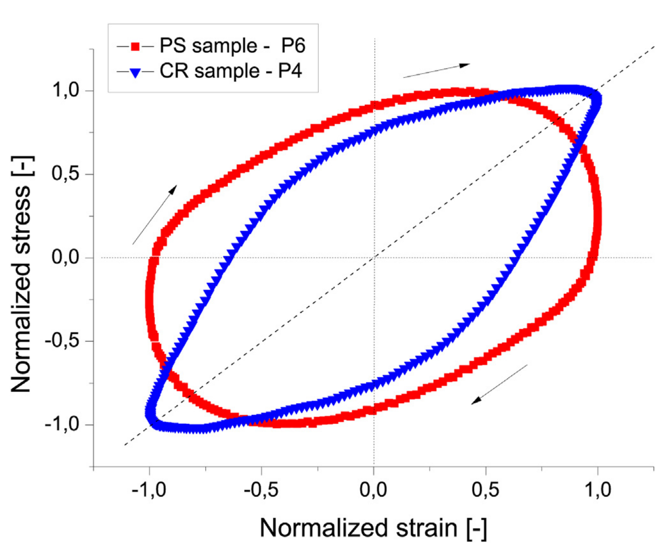

Fig. 10. Normalized Lissajous figures corresponding to the maximum of G'' for CR and PS samples at $\omega = 1$ rad/s, see Fig. 1.

property. If what we observe is a manifest of slipping, it means that slip at the boundary (for a given boundary geometry) is independent on the type of applied test and on the history of deformation. We consider the first explanation more plausible.

In Fig. 12 are shown three oscillatory amplitude sweeps tests for the CR sample which disclose very similar qualitative/quantitative results: same location of the yield point as the previous findings, i.e. $\gamma_{cr} \cong 0.23$ and $\sigma_0 \cong 80$ Pa. Here is also observed the second plateau corresponding to a stress value of $\sigma_1 \cong 250$ Pa, Fig. 3.

Same values of the shear stresses corresponding to the plateaus determined in simple shear are associated to the change in the topology of the Lissajous figures from Fig. 13.

Fig. 14 presents frequency sweeps performed in MAOS domain. The correlation between tests is very good if the existence of a plateau in shear stress amplitude vs. strain amplitude is assumed: at $\sigma_0 = 100\ Pa$ the strain controlled test is characterized by $\gamma_0 = 1$ and the stress controlled gives a deformation amplitude of $\gamma_0 = 0.2$, data which are consistent with results from Fig. 12.

The decompositions of the output signal using the FT-rheology are shown in Fig. 15. The tests were performed with and without the DSO system, using for the stress input test (Fig. 15a) the wave analysis modulus from the Physica MC 301 rheometer.

The performed experiments emphasize the following aspects: (i) a sharp increasing of the third harmonic within the MAOS regime (more than 10% from A1 at strain amplitudes higher than γ_{cr}), (ii) the maintaining of the second harmonic generally below

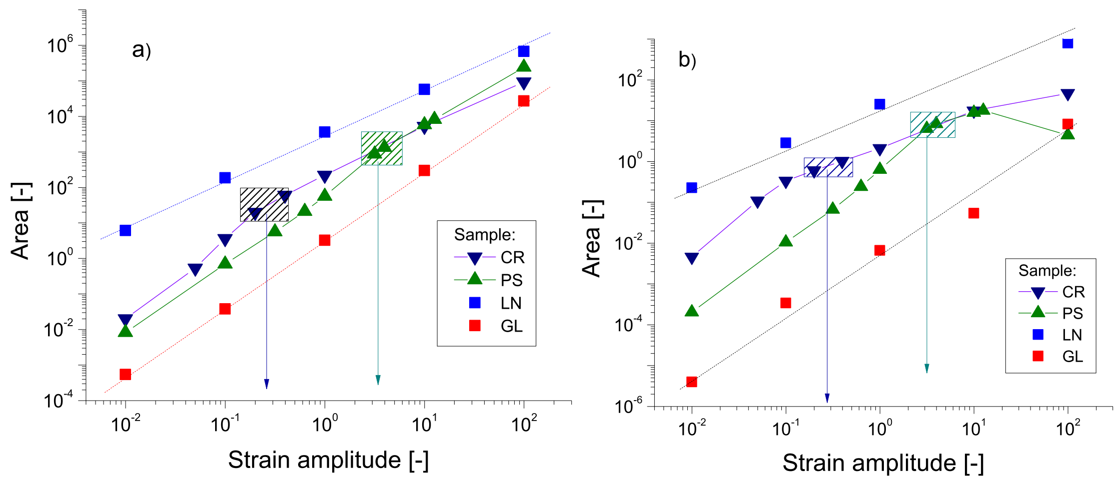

Fig. 11. Area of Lissajous figures *vs.* strain amplitude for the tested sample, see Fig. 1; a) oscillatory stress *vs.* oscillatory strain; b) oscillatory stress vs. oscillatory strain rate ($\omega = 1\ rad/s$).

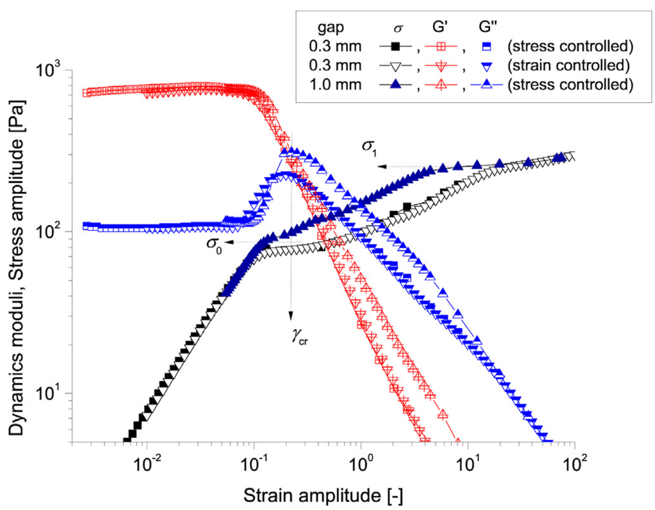

Fig. 12. Answers of CR sample in oscillatory tests under different experimental conditions (strain/stress amplitude sweep at $\omega = 1$ rad/s), see also Fig. 1.

1% from A1 for all regimes (with exception of the data extracted from the frequency sweep test at very small amplitudes). The increasing of the third harmonic is not monotonous in MAOS regime, which suggest the existence of the plateau in the flow curve. The existence of the second harmonic at relative amplitudes lower than 1% is normal for measurements performed with standard equipment. However, the data at low values for frequency sweep conditions (Fig. 15b) might suggest not necessary the existence of slip [56], especially if the material is characterized by non-monotonic constitutive relation [31,57,58].

The relation of yield state with the non-monotonous characteristic of the flow curve [22,31,51,52,59] respectively the possible competition between phenomena as slip and shear banding [19,21,23,24,27,60–63], seems to have a better understanding and explanations in the frame of MAOS and LAOS investigations techniques [7,35,41,42,64]. The rheology of soft matter is dominated by these phenomena and the present work is coming to support the developing of oscillatory techniques out of the linear regime, in order to obtain a better insight of the material behavior at the onset of the flow.

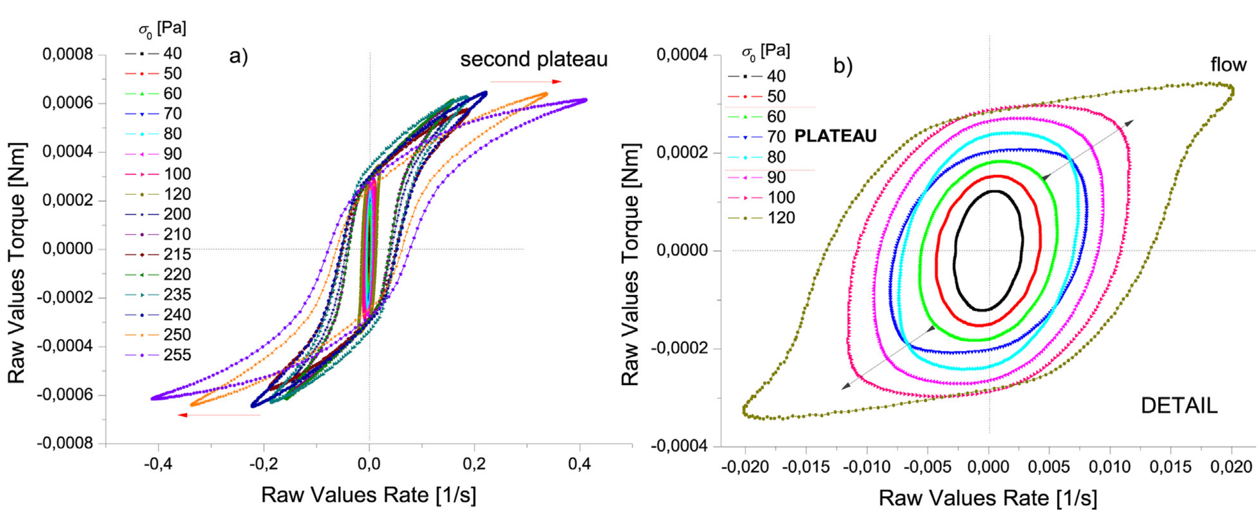

Fig. 13. The evidence of plateau behavior in the topology of Lissajous figures stress *vs.* strain rate for CR sample: a) well defined flow behavior at $\sigma_0 > 100\ Pa$, b) detail with the transition/plateau domain (input stress amplitude tests at $\omega = 1\ rad/s$), see also Figs. 3 and 12.

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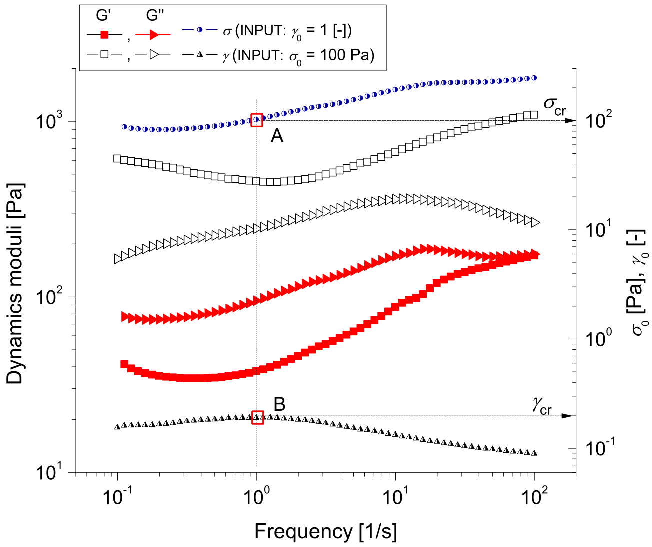

Fig. 14. Frequency sweep (controlled strain and controlled stress experiments) for CR sample. The corresponding values of loss tangent are: $\tan\delta = 2.6$ (point A – controlled strain), respectively $\tan\delta = 0.52$ (point B – controlled stress).

rheological behavior and indicates the onset of the flow.

The yield state is direct associated with the existence of the plateau in quasi-steady flow curve, which is in many cases the consequence of a non-monotonic constitutive relation [7,31,57]. This constitutive relation is unstable and normally generates shear bandings or kinks in the velocity distribution, phenomena which is not trivial to be distinguished from the real slip of the sample at the wall (especially if the slipping is located at nano- or micro-distances from the wall), [20,21,28,63]. We consider the oscillatory rheology an useful technique to investigate not only the existence of the plateau behavior and yield state, but also the presence of real slip phenomena [35,44,65,66]. In the absence of a specialized visualization system that allows a clear determination of the slip during our rheological experiments, oscillatory tests in MAOS and LAOS have potential to provide a better characterization of the wall depletion phenomena (which includes slip). If the plateau in shear curve is not quantitatively correlated with the data from oscillations, the most probably explanation is the existence of the real slip at the tool of the rheometer and not the presence of a yield state, [41,54,55]). This is not the case of the work from this paper.

The results of our study demonstrated that for materials in which the yield state is present, the correspondence between the

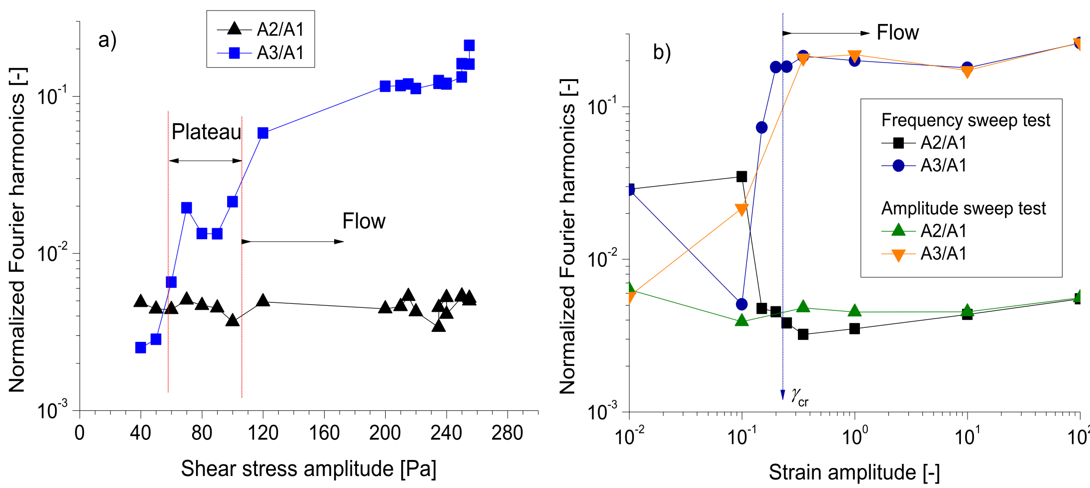

Fig. 15. The normalized Fourier harmonics extracted from stress input (a) and strain input (b) tests at $\omega = 1\ rad/s$. The results show the same interval for critical values of strain/stress amplitudes corresponding to the onset of the flow.

4. Conclusions

In this paper, we presented the rheological investigations of two soft matter samples in oscillation and simple shear flows. The tested materials, a cosmetic cream (CR) and polysiloxane (PS), disclose a well-defined yield state characterized by a critical value of strain deformation, γ_{cr}, which corresponds to the peak of the viscous modulus G'' in the strain sweep amplitude experiments and with the plateau shear stress in the flow curve.

Multiple oscillatory testes performed in non-linear regimes offer value information about the insight rheology of the samples, which in these cases are quantitatively confirmed by the data measured in shear.

One concludes that all results obtained for the two samples in simple shear and oscillatory flows are consistent with the existence of a yield state which delimitates the upper limit of linear simple shear and oscillatory tests can be established. Therefore, the onset of the flow, mainly observed in shear, is also detectable in oscillations and is associated to the transition from MAOS to LAOS regimes. The measurements from the dynamics controlled strain and stress tests are analyzed using the FT-rheology procedure and emphasis a clear threshold in strain amplitude for the onset of the flow. The results are also consistent with the topology of the Lissajous figures. The location of the yield point coincides with the strain amplitude corresponding to the peak in the viscous modulus located in MAOS regime, so the yielding behavior is better characterized by a critical value of strain, rather than a unique value of the yield stress.

The existence of material instabilities or/and slip in shear flows during solid-fluid transition of soft matter systems is still an open subject and also a challenge for developing novel techniques in rheometry and flow visualizations.

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