Rheology of Poly(vinyl chloride) Plastisol: Effect of a Particular Nonionic Cosurfactant

A. Tomás,[1] M. G. Rasteiro,[2] L. Gando-Ferreira,[2] S. Figueiredo[2]

[1]*Companhia Industrial de Resinas Sintéticas, Development, CIRES, S.A., Estarreja, Portugal*
[2]*Department of Chemical Engineering, Coimbra University, Coimbra, Portugal*

Received 19 November 2008; accepted 23 June 2009
DOI 10.1002/app.30998
Published online 8 September 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The rheology of poly(vinyl chloride) plastisols is affected by many aspects of the formulations, such as type and concentration of each component, temperature and, perhaps most important, the polymer properties. Taking into consideration the surfactants normally present during the polymerization reaction, in this work, a different approach was followed. Besides the usual polymerization surfactants, a particular ester-type emulsifier was also added in a postpolymerization stage. The results show a particle aggregation effect in the initial aqueous dispersion (latex) that promotes a significant decrease in the viscosity level, aging profile, and different viscoelastic properties of the latter plastisols. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 599–607, 2010

Key words: PVC plastisol; cosurfactant; viscosity; aging; particle size distribution; oscillatory rheometry

INTRODUCTION

The poly(vinyl chloride) (PVC) plastisol or paste is a dispersion (suspension) of fine polymer particles in a liquid plasticizer. Some other additives can be added, like thermal stabilizers, fillers and pigments, according to the requirements of the final product and application.[1]

Traditionally, the polymer is obtained by the emulsion or microsuspension methods, making the so-called dispersion polymer grades. In the case of emulsion process, the polymerization reaction is carried out in the presence of a free radical initiator, a monomer, and a surfactant in an aqueous media.[1,2] Typical surfactants, used in the case of vinyl chloride monomer, are anionic type, like sodium alkyl sulfates and sulfonates. However, some neutral surfactants are often added, during or after the polymerization step, to increase the emulsion stability or to give or improve other properties of the plastisols and end products.[3]

The final polymer particles, that can have a mean diameter from 0.1 to 1 μm, are normally spray-dried. During this stage, an aggregation effect is normally observed producing larger particles, with a mean diameter that can exceed 15 μm.[2]

The plastisol is industrially produced by an intensive homogenization of all the components, followed by deaeration to eliminate the entrapped air. After preparation, the paste is normally applied over a substrate by spread coating or, otherwise, cast or slushed into a mold.[1] In all cases, the rheological behavior of the plastisol is a key parameter of the processing optimization.

Therefore, several authors have been studying many aspects, which influence the plastisol rheology, such as solids concentration, temperature, particle size and size distribution, and plasticizer type.[2,4–10]

A particularly important phenomena, which affects the plastisol rheology through time, is the so-called "aging effect," related to a viscosity increase since the moment when it was freshly prepared. This increase is attributed to a mechanism where, simultaneously, particle deagglomeration, particle swelling, solvation, and dissolution coexist.[7] Therefore, the morphology and nature of the aggregates are deeply linked to the viscoelastic behavior of the plastisols through time, because the most friable aggregates are quickly deagglomerated by the high solvent effect of the plasticizer.[4,5,9,10] As the plasticizer penetrates the aggregates, the available volume fraction of liquid decreases and, simultaneously, the plasticizer effect is enhanced by the increase in the overall surface area of the polymer.

The type of emulsifier used in the production process may influence the paste rheology and "aging" rate, through its effect on the redispersion of the

Correspondence to: A. Tomás (arnaldo.tomas@cires.pt).
Contract grant sponsor: FCT; contract grant number: SFRH/BDE/15534/2005.
Contract grant sponsor: FCT; contract grant number: POCI/EQU/47024/2002.

particles after drying, which dictates the type of agglomerates.[2,10] Also, the emulsifiers added after polymerization, the so-called cosurfactants, can affect the plastisol behavior by enhancing the original surfactant effect or improving other particle's properties.[3]

The objectives of this work are to study the effect of a particular type of a nonionic cosurfactant, sorbitan ester, added after the polymerization stage, in the particle size distribution (PSD) of the polymer powder and, later, in the plastisol, correlating it with the correspondent rheological behavior through time.

EXPERIMENTAL

There are many types of sorbitan esters produced with different kinds of fatty acids and various degrees of esterification. Those are generally used as emulsifier for cosmetics. In this particular application, an effective water in oil emulsifier, with a low hydrophilic-lipophilic balance (HLB) was selected, in the assumption that the higher affinity of the surfactant with the water insoluble polymer would be of great interest to increase its effect over the particles.

Emulsion PVC samples

In the first step, PVC emulsion samples in the latex form, produced in industrial reactors, were collected from Companhia Industrial de Resinas Sintéticas, CIRES, S.A., located in Portugal.

Five latex samples were considered, the first one for reference and the other four with increasing dosages of the cosurfactant (sorbitan monolaurate, SML), 0.5, 1, 2, and 3% (w/w), referred to the PVC solids mass in the initial latex. All samples were dried in a Niro (Mobile minor®) spray dryer with 150°C of feed air temperature.

Other materials

A commercial grade of SML with a HLB of 8.6, purity of minimum 99.0%, was acquired from Hunstmann Corp., French plant, to use as a cosurfactant in a postpolymerization stage.

The plasticizer used in the plastisol formulations was diisodecyl phtalate (DIDP), trade name Palatinol® 10P from BASF GmbH, located in Germany (Density: 0.962 $g.cm^{-3}$; viscosity at 20°C: 120 mPa s). The organic solvent *n*-heptane (commercial grade) was used to dilute the plastisol before the PSD analysis.

TABLE I
Emulsion PVC Samples

E-PVC sample	SML (% w/w solids)
E-PVC 1	–
E-PVC 2	0.5
E-PVC 3	1.0
E-PVC 4	2.0
E-PVC 5	3.0

Transmission electron microscopy

The PVC latexes were diluted with deionized water until the proper concentration was obtained. A sample of the obtained diluted latex was sprayed directly to a transmission electron microscope TEM grid to get a uniform film. The grid was examined by using an electron microscope JEOL JEM-100S, and the TEM images were acquired with a camera.

Plastisol samples preparation

Commercial formulations of 50 phr of DIDP (parts of plasticizer per hundred parts of polymer) were prepared. The preparation of the plastisols was carried out in a planetary mixer during 15 min to obtain a homogeneous final paste. While aging proceeded, the paste was kept in a closed chamber at constant temperature (23°C) and relative humidity (≈35%).

Particle size distribution

PSD was measured by the laser diffraction technique (LDS), Mastersizer 2000, Malvern Instruments, UK. LDS was used to measure the PSD of the dry PVC powder in a diluted dispersion with *n*-heptane. Regarding the plastisol samples, according to the already published method,[8] the dilution procedure was also made with *n*-heptane.

Rheology measurements

Rheological measurements were conducted in a controlled stress rheometer, Model RS1, Haake, with a cylindrical sensor system Z34 DIN that comprises one rotor and one beaker, connected to a thermocontroller recirculation bath (constant temperature 23°C). The spindle used had 20 mm (radius) at a clearance to bottom 7.2 mm. For the plastisol samples, flow and dynamic tests were performed.

The flow tests allow one to characterize the rheological behavior of the pastes supplying information about the resistance to flow, a fundamental parameter to tune the final application conditions of the paste. Namely, the hysteresis area can provide useful information about the nonideal behavior of the paste, that is, of how resistance to flow will vary

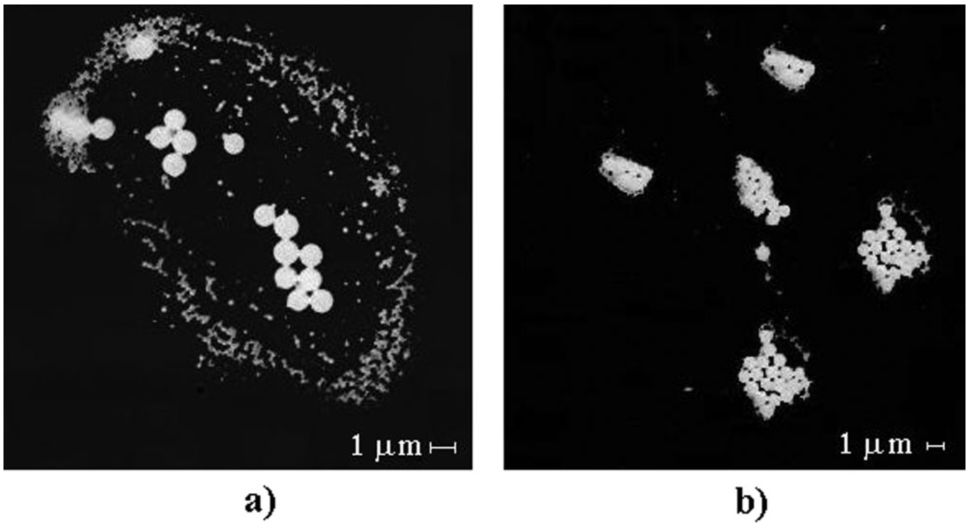

Figure 1 Representative TEM micrographs of latex samples (Magnification: ×2100): (a) E-PVC 1 (reference) and (b) E-PVC 5 (3% w/w SML).

under fixed shearing conditions applied over a certain time span. This information can also be extracted when the paste is subjected to an ascendant shearing ramp followed by a descendent one. When the two curves do not coincide the deviation between them is referred to as hysteresis.

The oscillating dynamic tests provide information about the viscoelastic nature of the sample and enable to describe the viscous and elastic components of the material, respectively, the viscous modulus (G'') and the elastic or storage modulus (G').[11] For that, frequency sweeps are conducted. For paste like materials $G' > G''$, for liquid like materials $G'' > G'$, and for solid materials, generally, it is also $G'' > G'$ but the relation between G'' and G' does not depend on frequency.[11] The frequency sweep has to be conducted for a stress in the linear viscoelastic region. So, to determine the linear viscoelastic range a previous stress test was made.

Through oscillatory rheometry, it is possible to characterize materials with complex structures that are not revealed by the flow tests. The relation between the two moduli, G'' and G', gives an indication of the structures that build up within the suspension and of the modifications in those structures as the result of the aging process.

The flow tests results presented here are the average of at least two samples, for each sample at least two measurements were performed.

RESULTS AND DISCUSSION

According to the experimental procedure, five emulsion PVC samples (E-PVC 1 to 5) were produced, as shown in Table I.

To evaluate the effect of the cosurfactant on the latex, TEM images were collected. In Figure 1, it is possible to analyze the differences between E-PVC 1 and E-PVC 5.

Considering the TEM micrographs, it is possible to conclude that SML induces an aggregation effect over the polymer particles dispersed in the water phase. A phenomenological explanation that can be advanced is based on the known lower aqueous affinity of SML droplets which, on the other hand, can be well dispersed in latex. As a consequence, they can act as an aggregation locus for the aqueous insoluble PVC.

Powder properties

After spray-drying all the latex samples, the correspondent five powder samples were collected and analyzed. In Table II are shown some parameters of the PSD, namely the d_{50}, the distribution ratios d_{90}/d_{10} and $(d_{90} - d_{10})/d_{50}$.

Considering the PSD parameters of all the powder samples (E-PVC 1–5), despite the differences in the SML dosage in the previous latexes, there are no significant differences in the d_{50} between all samples. Nevertheless, the ratio d_{90}/d_{10} increases from the reference sample (E-PVC 1) to E-PVC 2–4 and, more clearly, in E-PVC 5. This result indicates a different

TABLE II
PSD Parameters of E-PVC Powder Samples

E-PVC sample	d_{50} (μm)	d_{90}/d_{10}	$(d_{90} - d_{10})/d_{50}$
E-PVC 1	22.74	4.1	1.4
E-PVC 2	18.93	6.5	1.7
E-PVC 3	20.61	6.0	1.5
E-PVC 4	20.37	6.9	1.7
E-PVC 5	20.83	7.4	1.0

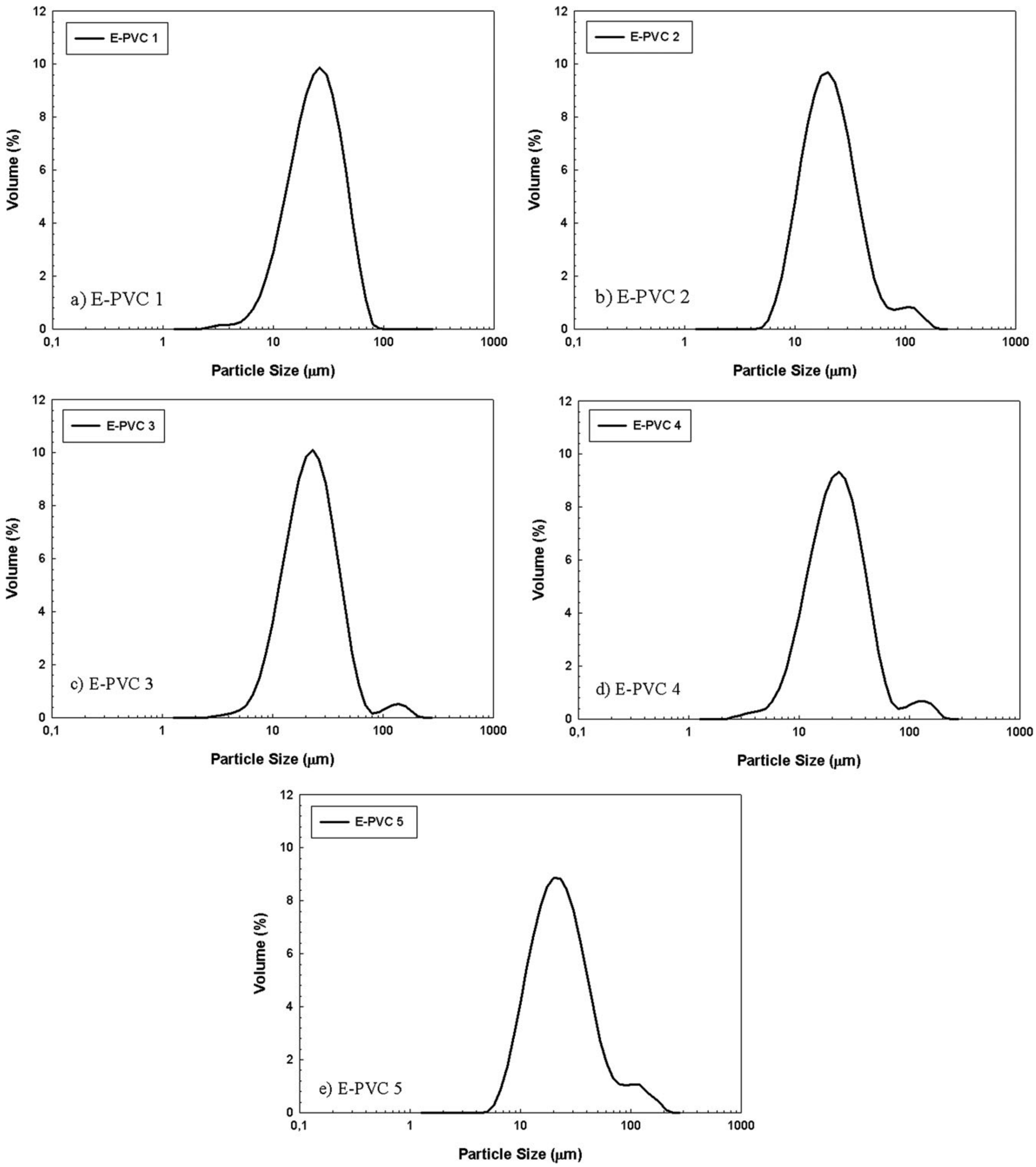

Figure 2 PSD distributions (from LDS) of powder samples E-PVC 1, 2, 3, 4, 5.

level of particle agglomeration of the final powder directly linked to the cosurfactant increasing dosage.

The ratio $(d_{90} - d_{10})/d_{50}$ can give an indication of the PSD variance that, besides the small differences from E-PVC 1 to E-PVC 2–4, decreases more pronouncedly in E-PVC 5. Thus, the increase in the aggregates fraction (larger d_{90}/d_{10}) of E-PVC 5 is followed by a correspondent narrower distribution with the disappearance of the smaller particles as can be observed in Figure 2(e).

Following the numerical differences between the samples in Table II, the PSD curves from Figure 2 give a more effective indication of the type of size distribution of each sample, namely the lower fraction of large aggregates of E-PVC 1 and the decrease in the fines fraction of E-PVC 5. Furthermore, in tune with the findings from the latex micrographs

(Fig. 1), it becomes evident from [Figs. 2(a,e)] the differences in the aggregation stage of the samples, namely between E-PVC 1 and E-PVC 5.

Plastisol's formulations

For each E-PVC sample, a plastisol (P1 to 5) was produced according to the referred procedure and formulation.

The aging rate and magnitude depends on several parameters, namely upon the solvent power of the plasticizer, temperature, and polymer properties. Nevertheless in the industrial practice, the time between the preparation and application of the plastisol is 1–2 days. Therefore, some control points are considered to define the correct process conditions of the paste (at room temperature). Namely, after 1, 3, 24, and, finally, 48 h to have a complete study of the paste samples.

Plastisol's PSD during aging

Considering the stated experimental procedure, Table III summarizes the PSD of the plastisols during the aging time from 1 to 48 h (2 days), after its preparation.

Comparing with the PSD results from the powder samples (Table II), there is a general decrease in d_{50} just 1 h after the plastisols preparation. This fact is mainly due to the high shearing conditions during preparation and, simultaneously, to the plasticizer solvent effect over the powder aggregates.

Excluding P1, there is almost the same d_{50} in P2 to P5. This effect is more evident in Figure 3(a), where P1 suffers significant changes in the PSD. In fact, after an early agglomeration effect from 1 to 24 h, at 48 h the larger fraction decreased, giving rise, nevertheless, to a higher median value due to the simultaneous decrease of the lower fractions. Moreover, for P1 to P3, there is an increase with aging time in d_{90}/d_{10} mainly due to the destruction of loose agglomerates for all the size ranges, but keeping the less friable ones [Fig. 3(a–c)].

Furthermore, for P4 and P5, the ratio d_{90}/d_{10} remains more or less constant with time, showing only a slight decrease, indicating the gradual destruction of the loose and larger agglomerates through the aging period which, however, are only a small percentage of the aggregates in the paste. Also, from Figure. 3(d,e), it is possible to see a more stable behavior in the PSD of the referred plastisols.

TABLE III
PSD of Plastisols During Aging

Plastisol	d_{50} (μm)				d_{90}/d_{10}			
	1 h	3 h	24 h	48 h	1 h	3 h	24 h	48 h
P1	12.48	13.30	14.50	18.47	10.6	13.3	16.5	30.2
P2	11.52	11.13	11.62	11.89	9.1	10.1	13.7	17.6
P3	11.04	11.24	11.54	11.42	8.9	9.3	11.1	12.0
P4	10.76	10.85	10.08	9.79	6.1	5.3	6.2	6.0
P5	10.32	10.58	9.49	9.57	7.7	5.1	5.5	5.5

Besides the observed effect in the latex, the cosurfactant effect over the aggregates morphology and size induces a different behavior of the PSD evolution of the plastisol. Again, these differences from reference (E-PVC 1) are more evident for a higher cosurfactant dosage (E-PVC 4 and 5).

Plastisol's flow properties during aging

The flow tests results in Table IV can be directly related with the observations made earlier regarding the PSD evolution. That is, the less compact the agglomerates on powder, greater the modifications on the paste state and on the observed increase in limit viscosity and hysteresis area through all the aging period. Moreover, an initial yield stress, which increases with age, can be found in plastisols P1, P2, and P3 (more pronouncedly in P1), which almost disappears in the case of the plastisols P4 and P5 corresponding to a higher surfactant dosage.

Thus, there is clearly a general decrease in the limit viscosity from P1 > P2 > P3> P4> P5 at 24 and 48 h. Also, the aging effect becomes less predominant from P1 to P5, even with a decrease in the limit viscosity, as time progresses, in P4 and P5. This off standard behavior can be explained by the small changes in the PSD of the referred plastisols, mainly due to the higher concentration of cosurfactant over the particles surface. The cosurfactant protection decreases the interaction between the particles layers and, perhaps more important, prevents the swelling and solvating effect of the plasticizer over the polymer particles. Therefore, in tune with the findings, it is possible to consider the cosurfactant SML with a significant effect as a viscosity aging depressant.

Considering the flow tests, for the same paste formulation, there is an increase in the hysteresis area through the aging period in P1 and P2. Also, plastisol P3 showed an unusual behavior exhibiting a too high hysteresis area, though not too different if we compare 1 h with 48 h. On the contrary, P4 and P5 have a constant behavior during aging, even with a slight decrease in the hysteresis area. Again, the existence of very compact aggregates in the latter plastisols induces a low hysteresis and a more Newtonian behavior

The differences on rheology are stated again in Figure 4, with the growing level of viscosity (μ) over the lower shear rate (γ) range applied to the samples (up to 10 s^{-1}): P1 >> P5. Moreover, the evolution of the rheological behavior, from a predominant pseudoplastic in P1, P2, and P3 to almost Newtonian in P4 and P5, due to the large number of compact aggregates, as explained previously, can be observed. Also,

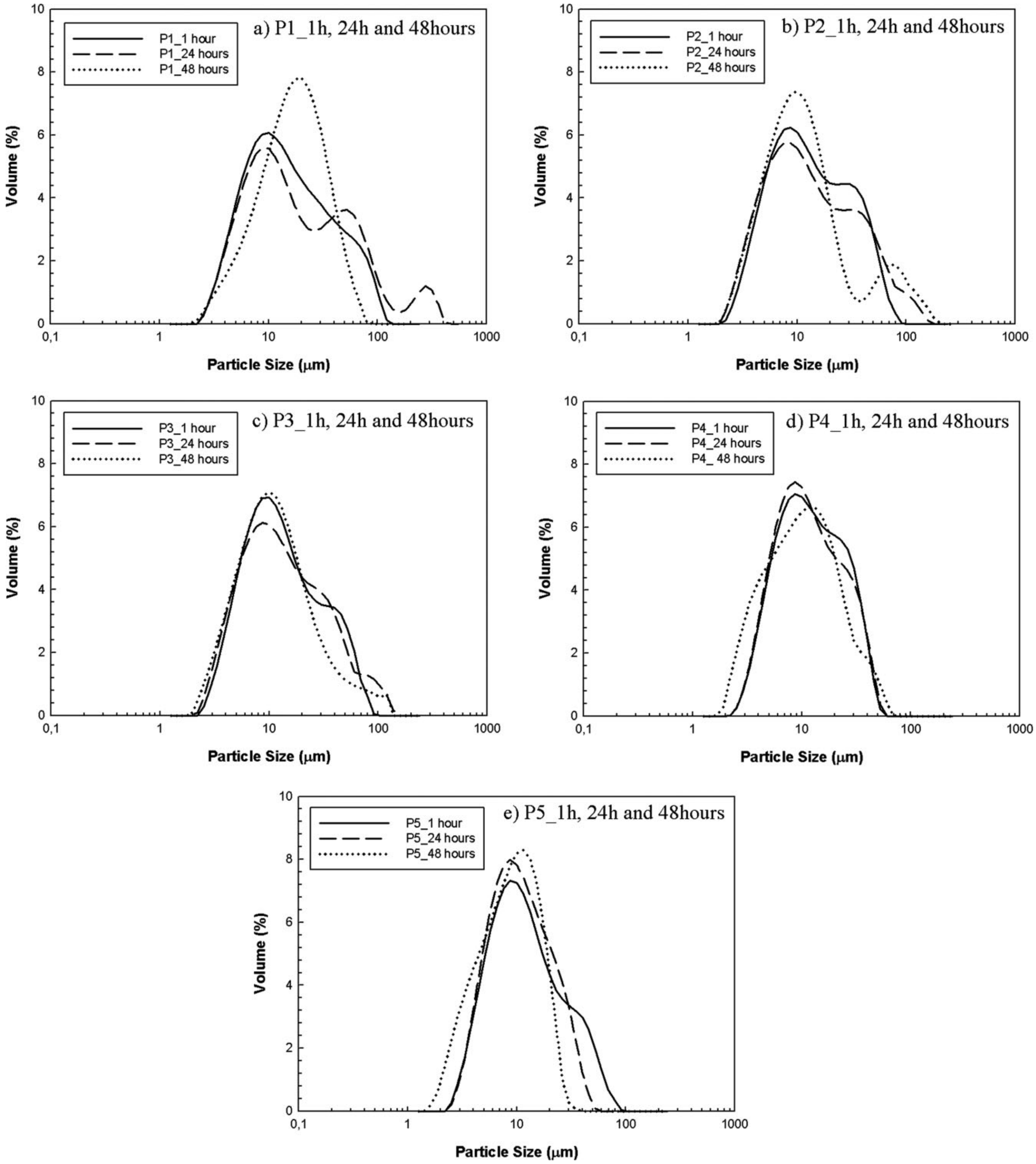

Figure 3 PSD distributions (from LDS) of plastisol samples P1, P2, P3, P4, and P5 for 1, 24, and 48 h.

the significant decrease in the aging effect through P1 to P2 and the constant behavior of P4 and P5.

Plastisol's viscoelastic properties during aging

The application of the oscillatory rheometry, through a frequency sweep test for a fixed stress, in the linear viscoelastic regime, allows a further evaluation of the material structure by the evolution of the two moduli (G' and G'') from 1 to 48 h.

Analyzing the dynamic results from Figure 5, in plastisols P1 to P4 there is a predominant elastic ($G' > G''$) behavior during the frequency sweep tests at 1 and 48 h, though, it is possible to see an evolution in behavior from P2 to P4 with a steady approach of the loss (G'') and storage (G') moduli. Also, it becomes clear the aging effect over the viscoelastic response, mainly with the increase in the storage modulus (G') versus the loss one.

TABLE IV
Flow Tests Parameters of Plastisols During Aging

Plastisol	Limit viscosity (Pa s)				Relative increase in μ (%)			Hysteresis/γ (Pa)			
	1 h	3h	24 h	48 h	3 h	24 h	48 h	1 h	3 h	24 h	48 h
P1	17.0	16.8	18.7	20.1	−1	10	18	8.6	9.0	12.2	11.8
P2	14.4	13.4	15.2	16.9	−7	6	17	6.0	4.6	8.9	9.6
P3	13.5	13.6	15.0	16.3	1	11	21	22.2	31.6	10.8	23.4
P4	17.6	14.7	14.0	14.1	−16	−20	−20	7.0	7.4	6.7	5.7
P5	14.2	13.3	12.6	12.0	−6	−11	−16	4.6	4.4	3.3	3.0

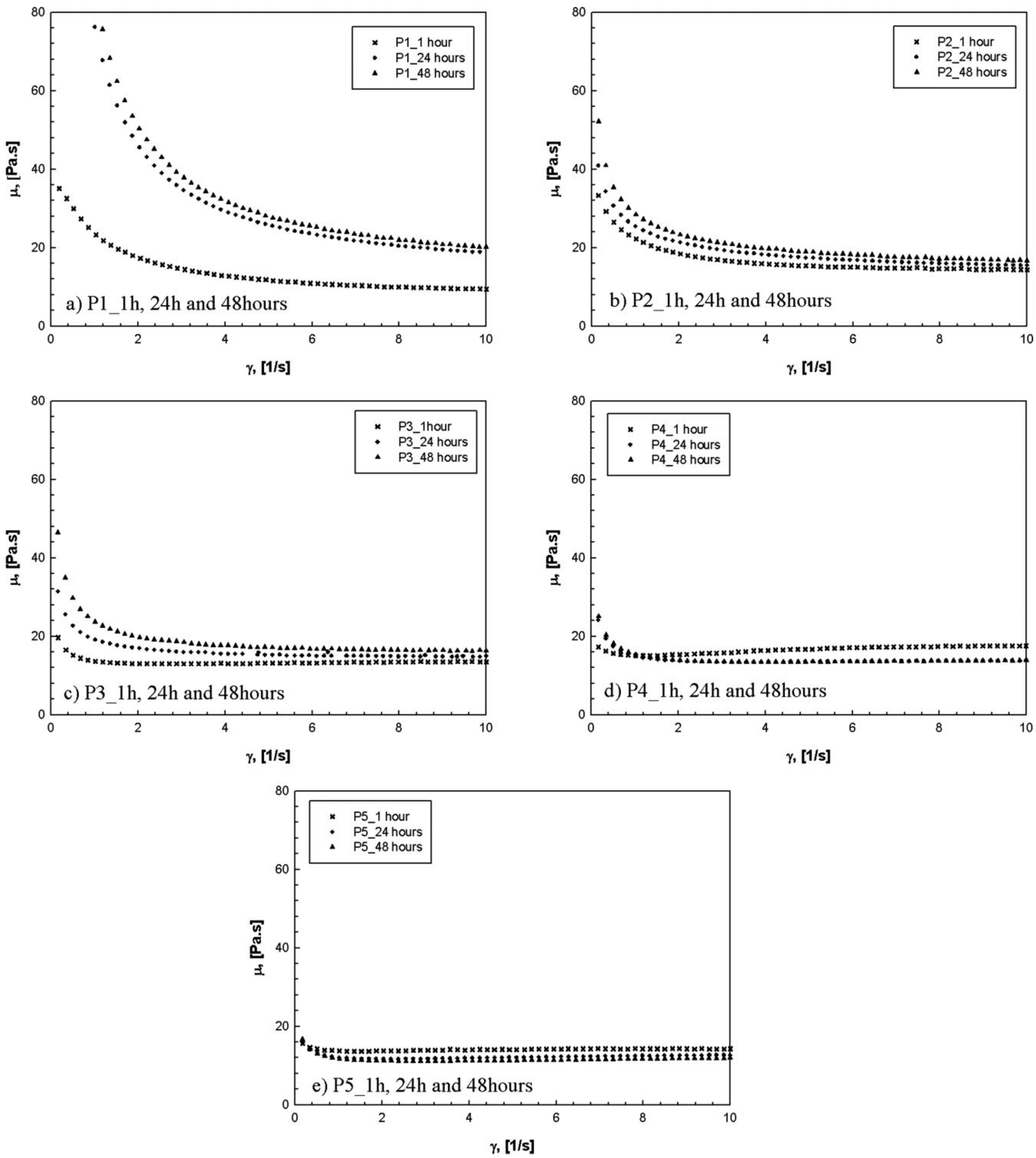

Figure 4 Viscosity versus shear rate for plastisol samples P1, P2, P3, P4, and P5 at 1, 24, and 48 h.

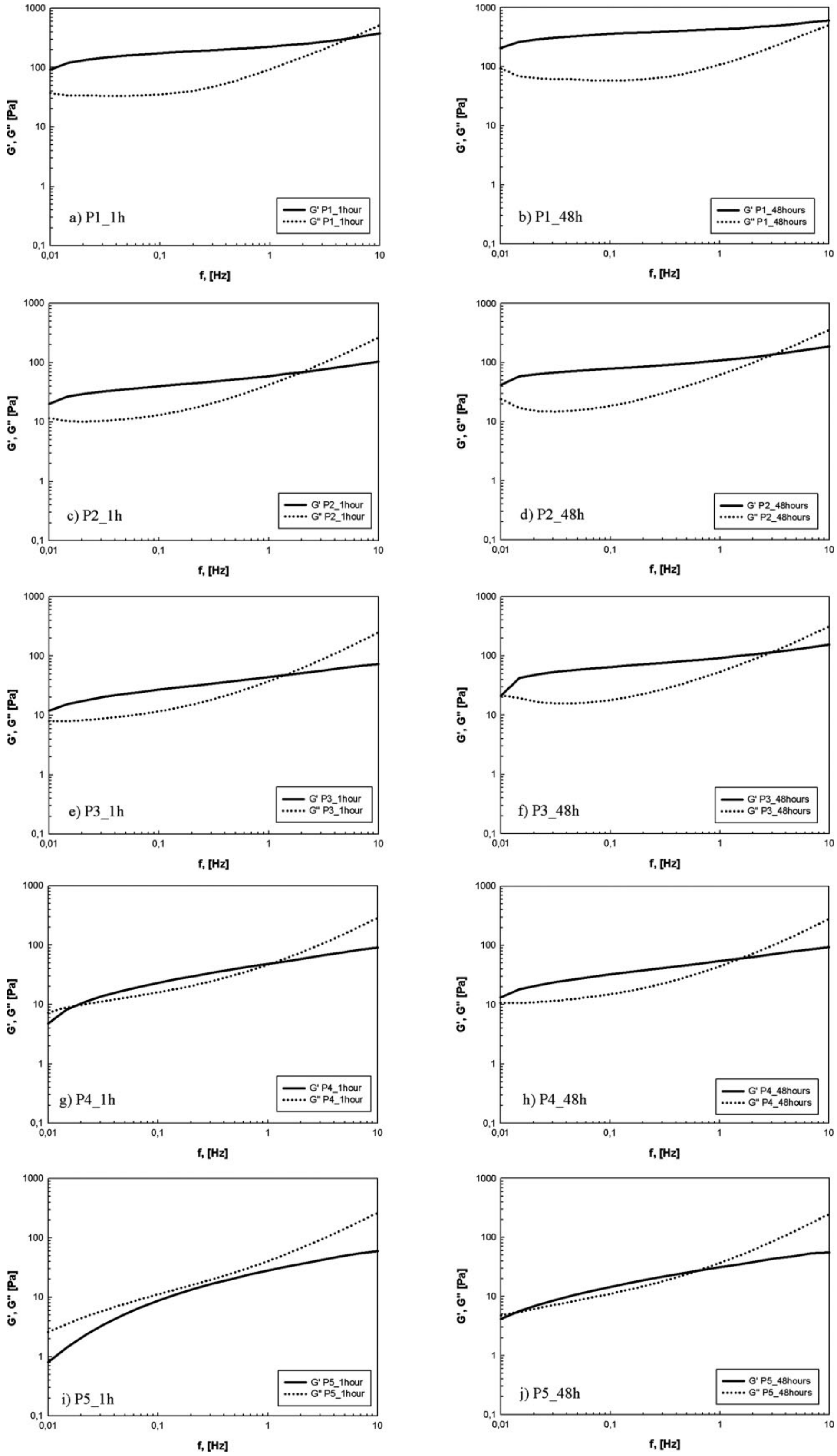

Figure 5 Dynamic tests of P1, P2, P3, P4, and P5 at 1 and 48 h: frequency sweeps.

Furthermore, with the increasing dosage of cosurfactant (P2 to P5), for both control points, the viscous forces (G'') seem to override the elastic ones (G') for lower frequencies. This result is more evident in P5 [Fig. 5(i,j)], because at 1 h the loss modulus is greater that the storage one ($G'' > G'$) for all the frequency range, with only a small difference in moduli at 48 h.

Correlating with the data from Tables III and IV, P5 shows the lowest hysteresis area and a small decrease of d_{50} just after the paste preparation. Moreover, due to the cosurfactant effect, the resin in P5 (E-PVC 5) is composed of many large structured and compact aggregates. Thus, just 1 h after the plastisol's preparation, the viscous forces still predominate ($G'' > G'$) due to the high number of large structured aggregates and the plasticizer availability in the mixture. As aging proceeds, there is only a slight modification in the moduli, with G' only slightly overriding G''. Plastisol P5, not only exhibits a quasi-liquid behavior, even after aging, but also presents quasi-Newtonian flow behavior.

Also, the PSD evolution during aging of P4 and P5 comparing with P1, correlates directly with the observed results in Figure 5(b,h,j). That is, the almost constant size distribution and the non friable agglomerates greatly contribute for a decrease in both moduli which, on the other hand, are similar between them ($G' \approx G''$), indicating that the elastic behavior is less important in these pastes.

CONCLUSIONS

The process conditions during the production of dispersion polymers are normally kept within the know-how of the industrial producers, namely the effect of a particular surfactant or additive in the quality parameters of the obtained final product.

Although the rheology of the plastisols has been quite analyzed, the work presented here aimed to study the effect of a particular surfactant type over the polymer particles in the latex and the correspondent effect in the viscosity of the latter plastisol. Furthermore, the LDS technique, applied directly to the plastisol, can give relevant information about the evolution of the PSD with time and, thus, about the interaction degree with the plasticizer and the strength of agglomerates.

The obtained results show that the addition of an ester of sorbitan with a low HLB can promote an aggregation effect in the latex that, clearly, will affect the rheological behavior of the paste. Thus, unlikely the reference sample (E-PVC 1), the limit viscosity of the plastisols with a small dosage of cosurfactant in the initial powder will be lower with a steady approach to a Newtonian behavior through the applied shear rate. On one hand, the cosurfactant leads to more compact aggregates which, once in the paste do not tend to degrade and, on the other hand, the cosurfactant protection interaction between the aggregates is reduced. Therefore, the typical aging rate can be almost cancelled with an interesting decrease in viscosity from 1 to 48 h with a minimum SML dosage of 2% (w/w) in E-PVC 4.

Concerning the dynamic shear tests, the results showed again that the cosurfactant can affect the viscoelastic behavior of the plastisols as a result of the different characteristics of the aggregates produced, mostly the storage component (G') from P1 to P5, in tune with the more stable PSD of P5 and the correspondent lower viscosity and approach to Newtonian behavior.

NOMENCLATURE

DIDP	Diisodecyl Phtalate
E-PVC	Poly(vinyl chloride) from the emulsion production process
f	Frequency, Hz
HLB	hydrophilic-lipophilic balance
LDS	Laser diffraction Technique
P1–5	Plastisol's samples
PSD	particle size distribution
TEM	Transmission electron microscopy
SML	Sorbitan monolaurate
d_{50}	Median of the particle size distribution, μm
d_{10}	Particle diameter corresponding to the 10% cumulative percentage, μm
d_{90}	Particle diameter corresponding to the 90% cumulative percentage, μm
G'	Storage modulus, Pa
G''	Loss modulus, Pa

Greek letters

μ	Newtonian viscosity, Pa s
γ	Shear rate, 1/s
τ	Shear stress, Pa

References

1. Sarvetnick, H. A. Plastisols e Organosols; Van Nostrand Reinhold Company: New York, 1972.
2. Nakajima, N.; Harrel, E. R. J Colloid Interface Sci 2001, 238, 105.
3. Ugelstad, J.; Mørk, P. C.; Berge, A. In Vinyl Chloride Polymerization; El-Aasser, M. S., Lovell, P. A., Eds. Wiley: New York, 1997; pp 590–618.
4. Collins, E. A.; Hoffman, D. J. J Colloid Interface Sci 1979, 71, 21.
5. Nakajima, N.; Harrel, E. R. J Appl Polym Sci 2005, 95, 448.
6. Nakajima, N.; Harrel, E. R. J Colloid Interface Sci 2001, 238, 116.
7. Hoffmann, D. J.; Garcia, L. G. J Macromol Sci Phys 1981, 20, 335.
8. Rasteiro, M. G.; Antunes, E. Particulate Sci Technol 2005, 23, 361.
9. Rasteiro, M. G.; Tomás, A.; Ferreira, L.; Figueiredo, S. J Appl Polym Sci 2009, 112, 2809.
10. Barroso, E. G.; Duarte, F. M.; Couto, M.; Maia, J. J Appl Polym Sci 2008, 109, 664.
11. Tanner, R. I. Engineering Rheology; Oxford University Press: USA, 2nd ed.; 2000.