

A Rheological Study of the Ageing of Emulsion and Microsuspension-Based PVC Plastisols

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ABSTRACT: A PVC plastisol is a homogeneous dispersion of PVC resin in a liquid continuous phase consisting basically of a plasticizer and a thermal stabilizer; the PVC resin being usually a fine powder is polymerized by emulsion or microsuspension processes. Plastisol rheology is affected by many aspects of the plastisol formulations, such as type and amount of each ingredient, the mixing procedure, temperature, and the effect of PVC resin properties. In this work, the

ageing behavior of PVC plastisols with different resin types was studied, with the results showing an unexpected behavior in the elastic modulus, probably originating from plasticizer adsorption at the surface of the PVC particles. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 664–673, 2008

Key words: PVC plastisol; microsuspension resin; emulsion resin; ageing; viscoelastic properties

INTRODUCTION

Plastisols are suspensions of PVC resins in a liquid continuous phase consisting of a plasticizer and a thermal stabilizer. Some additives, like pigments, rheology modifiers, and fillers, can also be added to modify the properties or decrease the plastisol price. PVC resins obtained by the emulsion polymerization process are traditionally used in the preparation of plastisols. The most frequently used plasticizers are phthalate esters, because of their good performance and relatively low prices comparatively with other kinds of plasticizers.^{1,2} Plastisols are commercially applied in coatings, films, sheets, and foams, made by roller or knife-edge coating, dip coating, rotational casting, slush molding, etc., and the final products are used, for example, in automotive applications, coated fabrics, and resilient flooring.^{3,4} Different processing methods require different flow behaviors from the plastisols. The industrial processing of plastisols involves the heating of the plastisol in an oven at about 180–200°C, and the plastisol undergoing two processes known as gelation and fusion.⁵ The viscoelastic characterization of the plastisol by means of small amplitude oscillation tests is an adequate method to study the gelation and fusion

processes, and the elastic (G') and the viscous moduli (G'') are the most frequently used parameters; however, the complex viscosity (η^*) and loss tangent ($\tan \delta$) can also be employed in the study of both processes.^{5,6}

The resins used in plastisols manufacturing are called dispersion resins and contain emulsifiers, the types of which will influence the performance of the final plastisol.³ Dispersion resins can be prepared by two different processes: emulsion and microsuspension. The main differences between the two processes are that in microsuspension polymerization, a monomer-soluble initiator is used and some or all of the monomer is emulsified to small droplets using mechanical means to initiate the polymerization.⁴ In the emulsion polymerization process, water-soluble initiators are applied and polymerization takes place either in the micelles or in water, where a certain amount of solvated monomer of vinyl chloride always exists.⁴ However, the elements and polymerization reactor used in both processes are similar. Because of (among other factors) the very low amounts of emulsifying agents present during the polymerization process of microsuspension resins^{7,8} by comparison with emulsion resin, the primary particles of the former are much more rigid than those of the latter; for example, because of this high rigidity and difficulty to melt, microsuspension resins are normally used to give a matte finish to PVC products.

Product quality of pastes obtained with resins from each process is different mainly because of the difference of particle size distribution. Both types of resins are made up of two kinds of particles:

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TABLE I
Plastisol Composition

Microsuspension PVC-based plastisol		Emulsion PVC-based plastisol	
100 phr PVC resin	100 phr PVC resin	100 phr PVC resin	100 phr PVC resin
50 phr DOP	70 phr DOP	50 phr DOP	70 phr DOP
1.5 phr thermal stabilizer	1.5 phr thermal stabilizer	1.5 phr thermal stabilizer	1.5 phr thermal stabilizer
0.5 phr UV stabilizer	0.5 phr UV stabilizer	0.5 phr UV stabilizer	0.5 phr UV stabilizer

primary particles, with an average diameter of about 1 μm , and secondary particles, which are the result of the agglomeration of the primary particles, with sizes up to 45 μm . If the polymerization process has been run under severe conditions, the secondary particles are broken easily and can be broken during the mixing process in the plastisol preparation.^{4,9}

Many aspects of the plastisol formulation, such as temperature and quantity of each additive, affect the rheology of plastisol; however, the properties of the PVC resin (molecular weight, amount of emulsifier, mean particle size, and particle size distribution) are the most important aspects. Mean particle size and particle size distribution of paste resin, which have a direct relation with production process, are the most important factors for controlling properties of plastisol. Generally large mean particle size produces low-viscosity plastisols.^{2,4} The viscosity of fresh PVC plastisol increases with time and this phenomenon is called viscosity ageing. The increase is rapid in the beginning and slows down to a quasistable value, although a very slow increase continues in time. The phenomenon may be the result of either the deagglomeration of agglomerated particles or the dissolution of low molecular weight PVC into the plasticizer.¹⁰ The rate and magnitude of the increase in the viscosity depend on the solvent power of the plasticizer and temperature. As for the latter, the ageing is much more significant at 40°C than that at room temperature.¹⁰

The main aim of this work is to study the ageing behavior of PVC plastisols made with both resin types and to relate the results to the structural characteristics of each resin.

EXPERIMENTAL

Materials

In plastisol preparation, two different grades of PVC resins with the same K values ($K = 70$) were used: an emulsion grade and a microsuspension grade. All the samples had the same type and amount of a phthalate plasticizer and light and thermal stabilizers, as shown in Table I.

Structurally, the two resins differ in terms of mean particle size and particle size distribution as can be seen in Figures 1 and 2, respectively.

The histogram of particle size distribution of the both resins was obtained by SEM and using the Image Pro Plus image processing software. The results show that microsuspension resin is essentially made up of primary particles and has, as expected,⁹ a relatively wide particle size distribution. In fact, the average primary particle radius is 0.7 μm and only 0.5% (in volume) of the PVC is in particles with average radius higher than 2.7 μm .

Conversely, the emulsion resin shows a clear multimodal distribution with a very narrow (between 0.6 and 1.5 μm) primary particles size distribution, but a very long tail of large secondary particles, i.e., agglomerates, by comparison with the microsuspension

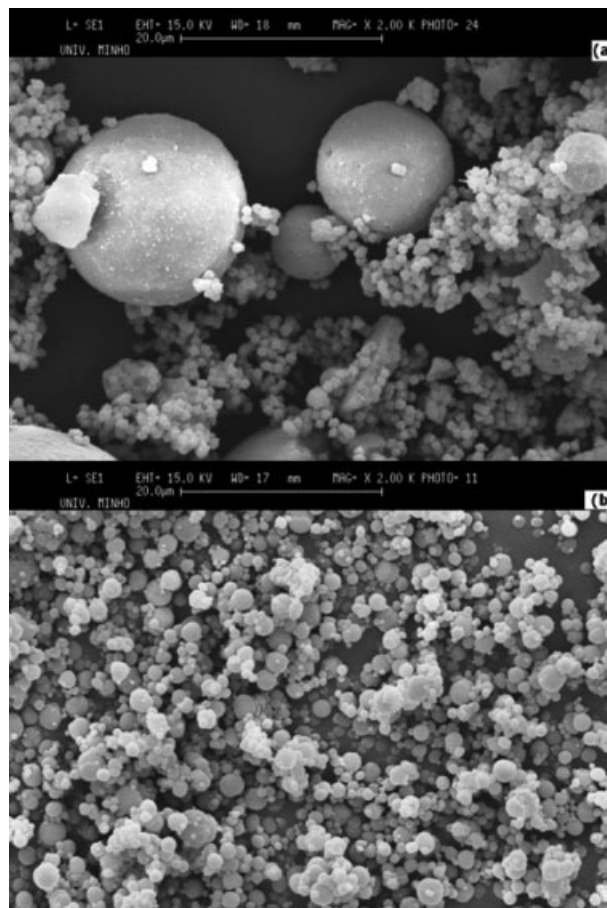


Figure 1 Morphology and particle size distribution of both resins: (a) emulsion resin and (b) microsuspension resin.

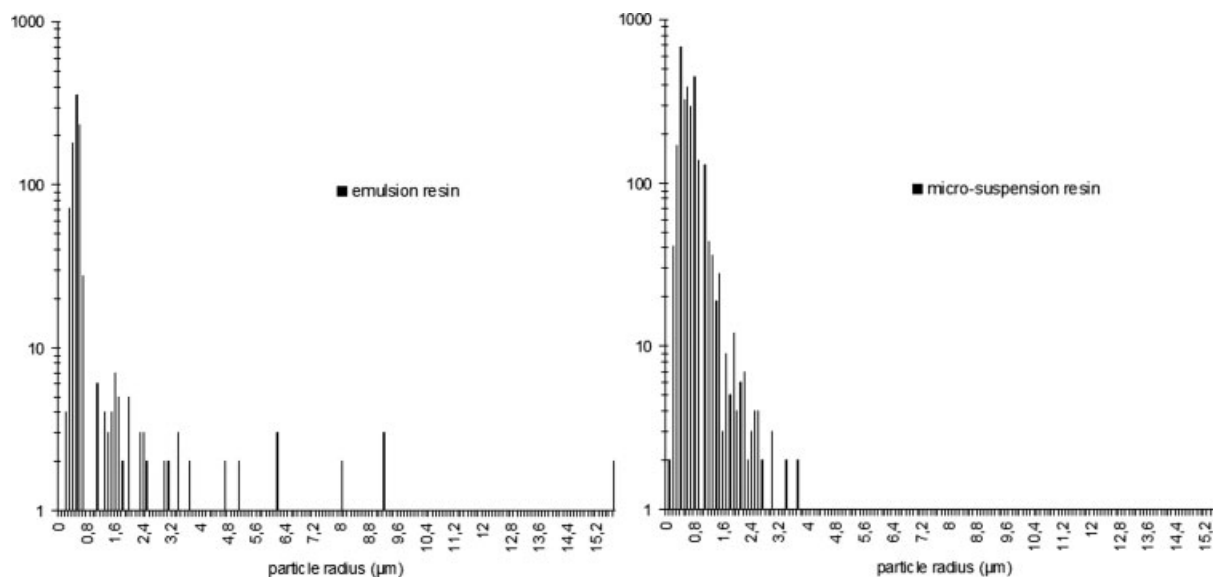


Figure 2 Histogram of particle size distribution of the both resins.

sion resin. For the emulsion resin, 5% in volume of the PVC is located in particles with average diameters higher than $2.7 \mu\text{m}$ while the largest have radii in excess of $15 \mu\text{m}$.

Methods

The PVC plastisols were prepared in a mixer during 20 min. The rheological studies were made in a rotational controlled stress rheometer in a parallel-plate configuration (Reologica Stresstech HR). The plates had a diameter of 40 mm, and the standard gap used was 0.8 mm. The linear zone of each sample was determined by means of stress sweeps in oscillatory mode at two constant frequencies (0.1 and 10 Hz) and the remaining tests were made with the parameters given in Table II.

To determine the range of linear viscoelastic response in oscillatory shear, stress sweep tests at fixed frequencies of 0.1 and 10 Hz were performed on all samples, as exemplified in Figure 3 for the emulsion based plastisol. For a frequency of 0.1 Hz the material had a linear response between 0.03 and 0.387 Pa, and for 10 Hz between 0.139 and 13.9 Pa. With this information the stress profile for the frequency sweeps was defined in order for the material response to be in the linear viscoelastic limit.

RESULTS AND DISCUSSION

In the industrial environment the time between the preparation and application of the plastisol is 1–2 days, sometimes it can be longer, but it is always less than 1 week. The ageing studies of the plastisols were made over a 1-month period (at room tempera-

ture) to cover the industrial interest adding simultaneously relevant scientific information about the ageing behavior of this type of products. Rheological measurements made on the different plastisols during this period were: fresh plastisol; after 24 h, 1, 2, and 3 weeks and 1 month. Visually, it was quite clear that significant differences between the emulsion and microsuspension plastisol aspect after 1 month (see Fig. 4).

This difference in plastisol consistency over time was confirmed by the steady shear tests results as depicted in Figure 5. In the emulsion plastisol both the viscosity and the apparent yield stress increase significantly with time, ranged from 0.15 Pa for the fresh sample to ~ 5 Pa after 1 month. On the contrary, the microsuspension plastisol keeps the same viscosity, apparent yield stress (0.15 Pa), and gelation behavior over the entire month but shows a shear-thickening behavior that is undesirable, for example, for coating applications.

The effect of the ageing on the gelation kinetics was also studied, the results being shown in Figure 6 for both types of plastisol. As can be seen, the gelation temperature of the emulsion-based plastisol increases by $\sim 12^\circ\text{C}$ during ageing, from 53 to 65°C ,

TABLE II
Parameters of the Different Tests

Viscoelastic tests	Frequency: 0.01–100 Hz 23°C 25 points
Shear tests	Logarithm shear stress: 0.03–2984 Pa 300 s (51 intervals) 23°C
Gelification tests	Temperature: 23 – 200°C at $10^\circ\text{C}/\text{min}$ Stress: 3 Pa

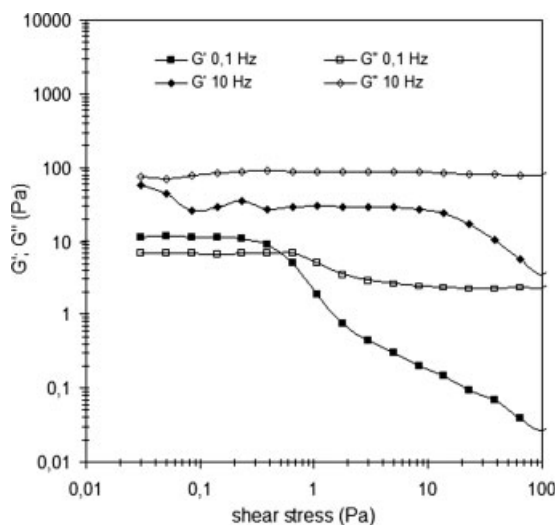


Figure 3 Stress sweep curves at fixed frequency for the emulsion based plastisol.

whereas the gelation kinetics remains by and large unchanged. Concerning the microsuspension-based plastisol, both the gelation temperature and kinetics is unchanged over time, the former being $\sim 20^\circ\text{C}$ higher than the emulsion-based plastisol gelation temperature.

Figure 7 shows the response of the materials in oscillatory shear and the results again show that, unlike the emulsion-based plastisol, the microsuspension one is very stable in time. In the emulsion plastisol, both the elastic (G') and viscous (G'') moduli increase significantly (~ 1 order of magnitude in 1 month) in time.

Figure 7 also shows an unexpected depression in the storage modulus, G' , of both plastisols in a frequency range between 3 and 20 Hz. This depression disappears after 1 week in the emulsion plastisol but not in the microsuspension. Also, it is clear from this figure that the effect exists in the G' curve only (and not in G'') and occurs before the onset of rheometer resonance (~ 30 Hz – shaded areas in Fig. 7). Given the proximity in frequency between the phenomenon and the onset of instrument resonance, it is important to assess if the phenomenon is not resonance related in some way. This can be assessed by the stress–strain response in terms of Lissajous curves at the frequencies of the phenomenon (Fig. 8). For the emulsion plastisol [Fig. 8(a)] and in the microsuspension plastisol [Fig. 8(b)], it is quite clear that the response is essentially linear, while at the resonance frequencies [Fig. 8(c)] the Lissajous curve are very different and the strain response is clearly nonlinear. Thus, there is no superposition between the effects.

To understand if the depression in the G' curve was a physical phenomenon or an experimental error several rheological tests were made, in oscillatory

mode, with different geometries (parallel plates with different gaps and surface finishes surface and cone-and-plate). Since all the tests were made with different samples of the same plastisol, by the last test the plastisols are already more than 1 h old and the ageing process has already started, especially in the emulsion plastisols (see Fig. 9). Because of that, and to dissipate the discrepancy of the results in the emulsion-based plastisols, all the G' curves are reduced response curves to that at 1 Hz.

Figure 10 shows the results for the storage and loss moduli of both plastisols under different experimental geometries and it is quite clear that the effect is present in G' for all conditions and both plastisols, which means that it is not due to experimental error, in all probability being a real effect.

Two extra plastisols, with 70 phr of plasticizer each, were prepared with the aim of assessing if the effect can be associated with the free plasticizer content in the plastisol. The results were compared with those for the base samples with 50 phr plasticizer and are shown in Figure 11, where it becomes clear that the effect is dependent on the amount of plasticizer, with the depression shifting to lower frequencies with increasing plasticizer content.

In addition, three successive frequency sweeps were performed on the same fresh samples of the base plastisols, i.e., the samples were not replaced in the rheometer by fresh ones between runs. The results of these experiments are shown in Figure 12 and show that in the microsuspension-based plastisol the behavior is totally reproducible, whereas in the emulsion-based plastisols intensity of the depression decreases with consecutive testing.

Finally, to investigate the influence of temperature on the effect, frequency sweeps were also performed at different temperatures, the results being depicted in Figure 13. For the emulsion-based plastisol, these

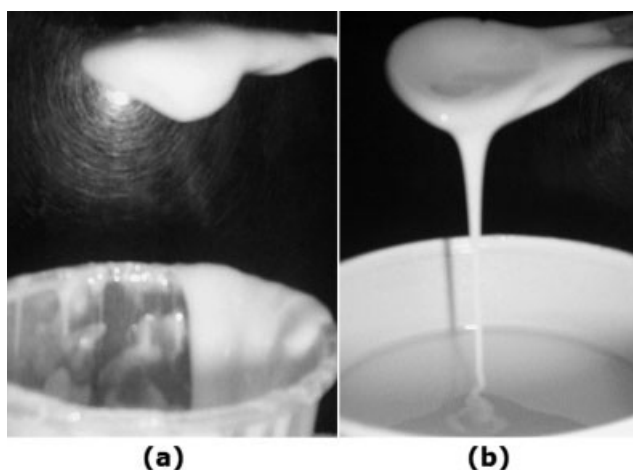


Figure 4 Plastisol aspect after 1 month for (a) emulsion-based plastisol and (b) microsuspension-based plastisol.

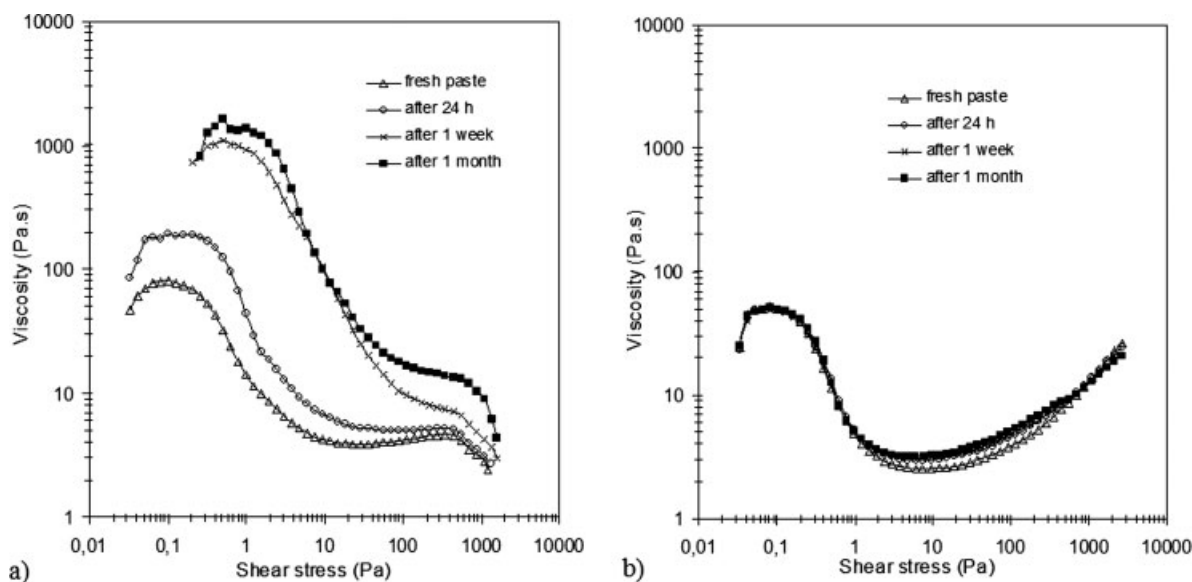


Figure 5 Flow curves for (a) emulsion-based plastisol and (b) microsuspension-based plastisol.

show that the effect becomes progressively smaller with increasing temperature, virtually disappearing above the temperature for the onset of gelation, i.e., $\sim 53^{\circ}\text{C}$. Conversely, in the microsuspension-based plastisol the effect is present up to 60°C , which is not unexpected since the onset of gelation for this fluid is $\sim 75^{\circ}\text{C}$. Thus, the effect seems to be dependent on the molecular mobility that decreases with the proximity of the gelation temperature.

Thus, the results show that this depression is

- very unlikely to be due to experimental error,
- a phenomenon related with the amount of plasticizer in the plastisol and with the molecular mobility, and

- most probably corresponds to a surface-softening only, without a significant change in the particle size because only the elastic response is affected, while the viscous one remains unaffected.

Both resins used in this work have the same k value, differing in the polymerization process and, consequently, essentially in terms of particle size distribution and particle rigidity. In the former case, the microsuspension resin is made up essentially of primary particles, while the emulsion resin contains a relatively large number of secondary particles (agglomerates). Regarding the latter, the particles of the microsuspension resin should be much more

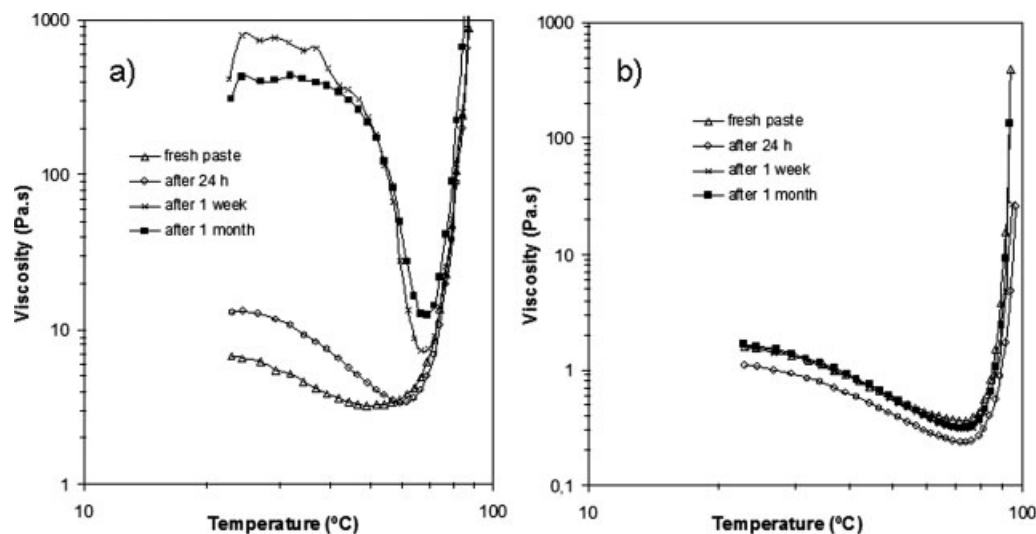


Figure 6 Gelation curves for (a) emulsion-based plastisol and (b) microsuspension-based plastisol.

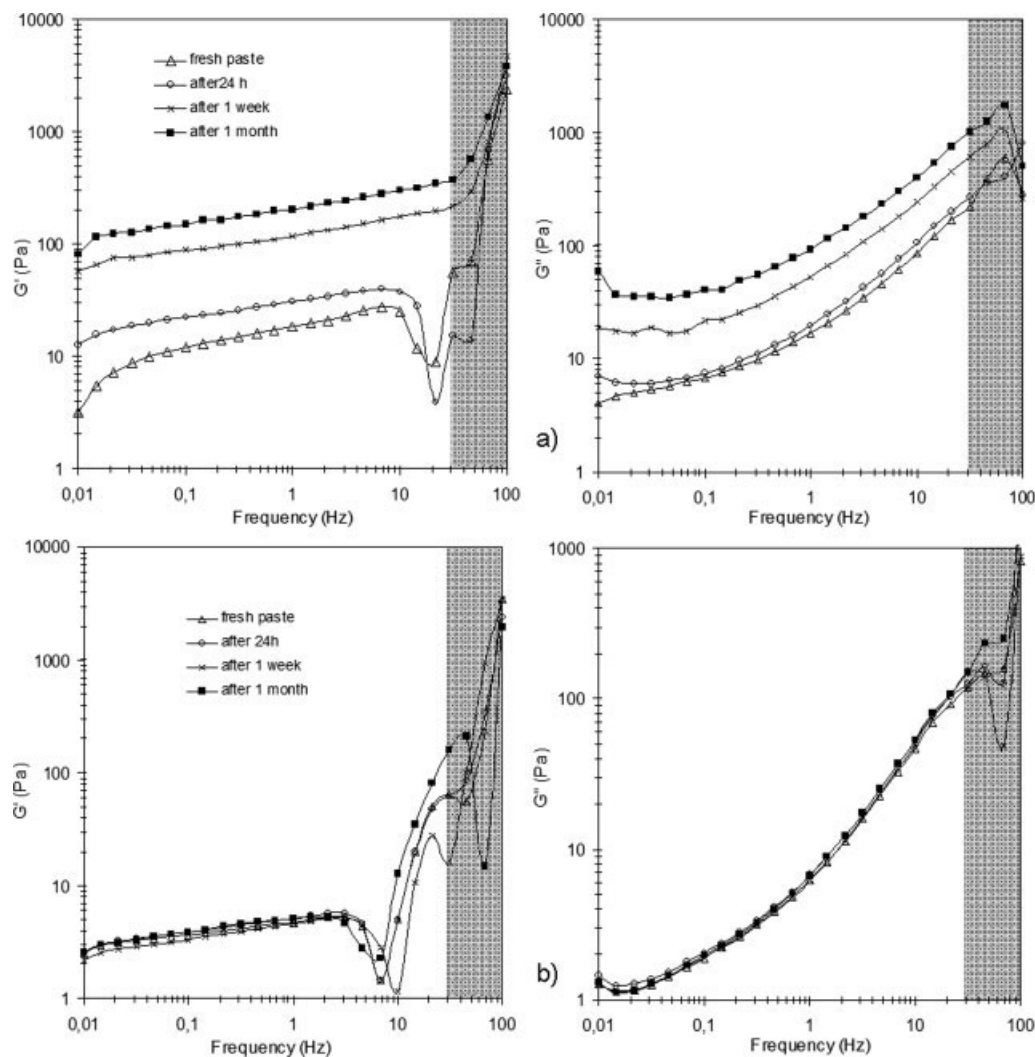


Figure 7 Linear viscoelastic behavior for (a) emulsion-based plastisol and (b) microsuspension-based plastisol.

rigid and less permeable to plasticizer action than those of the emulsion resin.

Analyzing the results, a pronounced depression in G' was observed, but not in G'' , at frequencies between typically 3 and 20 Hz, depending on the type of plastisol. Once it was established that this was not an experimental artifact, an explanation for it was required and the most likely cause is adsorption of plasticizer onto the surface of the PVC particles, i.e., the beginning of plasticizer diffusion into the PVC particles. This would then result in a decrease of the rigidity of the surface of the PVC particle, which would explain the drop in G' , but would not affect the bulk of the particle, which would explain the fact that there is no effect on the viscous response. Presumably, in the microsuspension plastisol, the plasticizer/PVC interface is very stable because of the inherent rigidity and low permeability of the PVC particles, which leads to weak and reversible interactions between the two. This

would explain the reversibility [Fig. 12(b)] and independence of temperature [Fig. 13(b)]. In the emulsion-based resin, on the other hand, the interactions between the plasticizer and the PVC are much stronger because of the lower rigidity and higher permeability (because of the incomplete shielding of the PVC by the emulsifiers of the particles) and also because of the fragility of the agglomerates present in the emulsion resin [particles with higher diameters that can be up to 15 times higher than the primary particles; see Figs. 1(a) and 2(a)], thus contributing to a much more diffuse interface and the beginning of the ageing process, i.e., of plasticizer adsorption onto the surface of the PVC particles. This would explain the partial short-term reversibility of the effect [Fig. 12(a)] and its disappearance when gelation begins [Fig. 13(a)]. One would also expect the effect to be dependent on the quantity of available plasticizer in both plastisols, which agrees with the behavior observed in Figure 11.

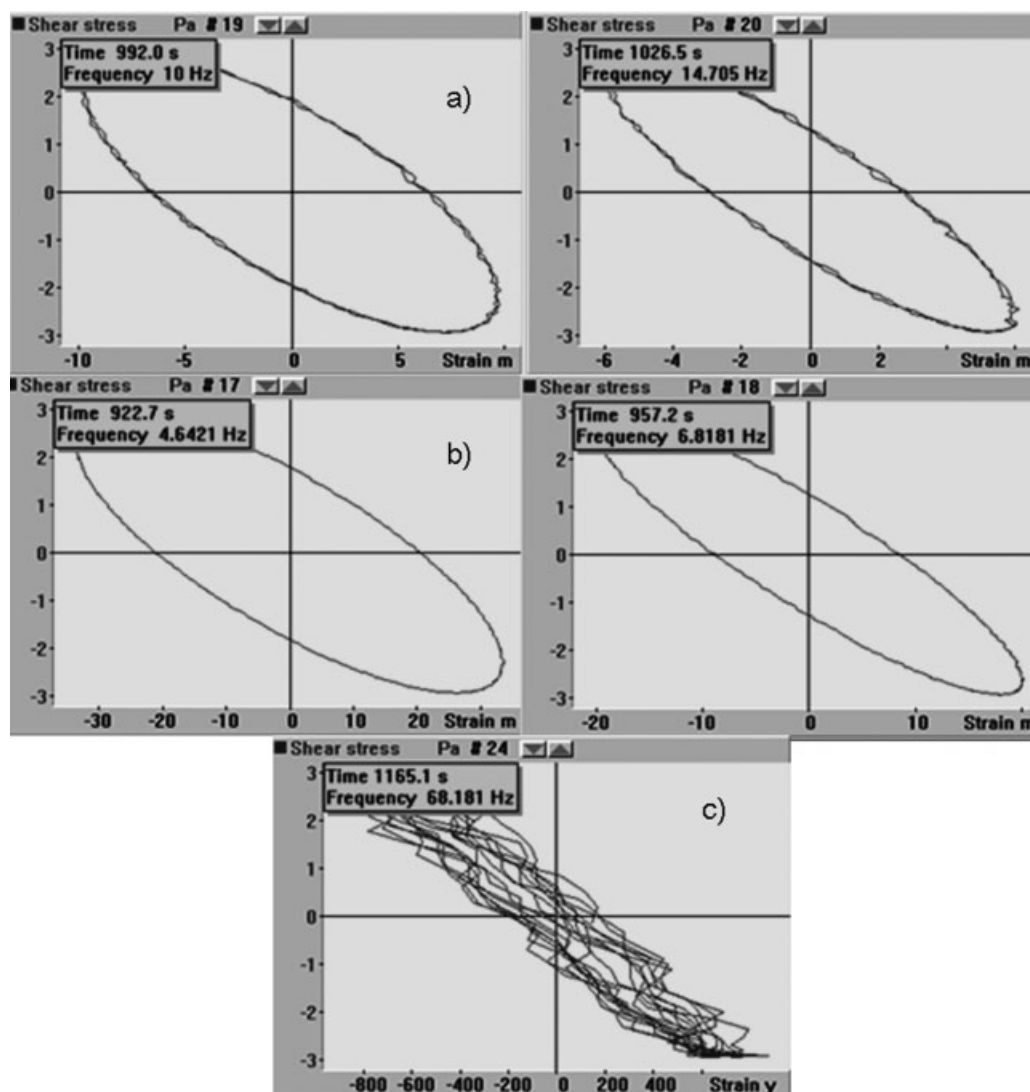


Figure 8 Lissajous plots of the stress–strain curves for (a) an emulsion sample at a frequency typical of the phenomenon, (b) microsuspension sample at a frequency typical of the phenomenon, and (c) emulsion sample at resonance.

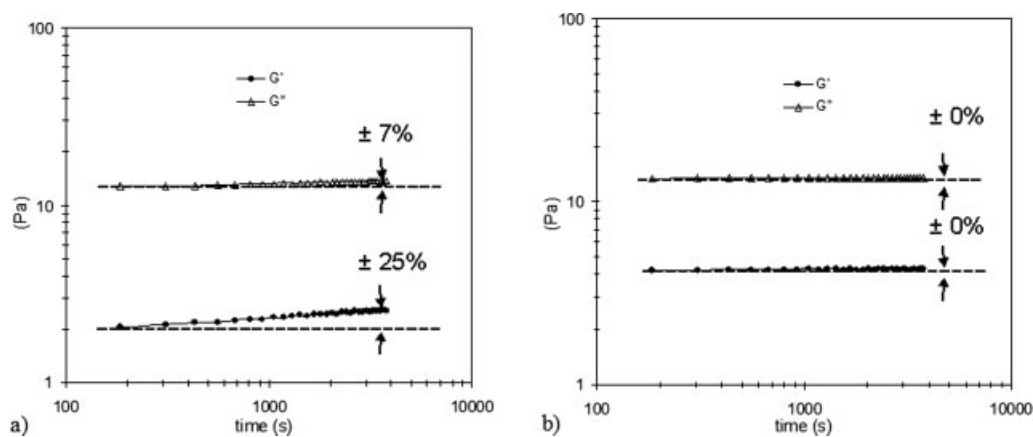


Figure 9 Short-term stability of the plastisols: (a) emulsion-based; (b) microsuspension-based.

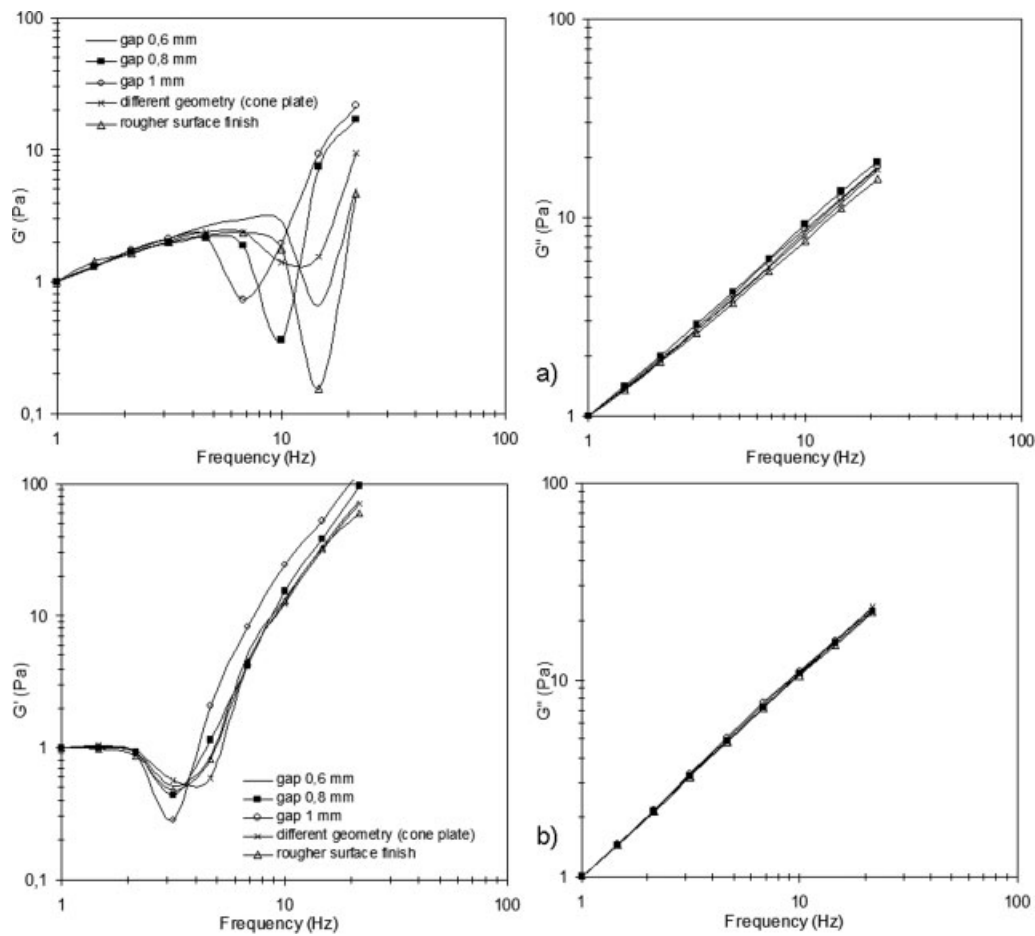


Figure 10 Linear viscoelastic behavior in different experimental geometries for (a) emulsion-based plastisol and (b) microsuspension-based plastisol.

In view of the analysis above, it is then possible to make use of this effect to gain an insight into how prone to ageing is a given plastisol or to differentiate between resin types in different plastisols simply by performing several consecutive frequency sweeps on the same sample and looking at

the evolution of the magnitude of the depression in G' .

CONCLUSIONS

The main aim of this work was to study the ageing of two PVC plastisols made from different types of

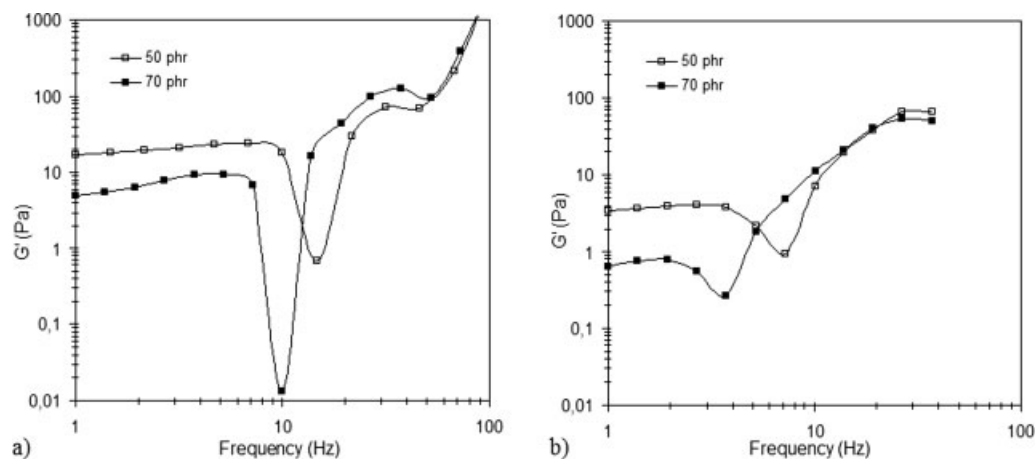


Figure 11 Linear viscoelastic behavior with different plasticizer content for (a) emulsion-based plastisols and (b) microsuspension-based plastisols.

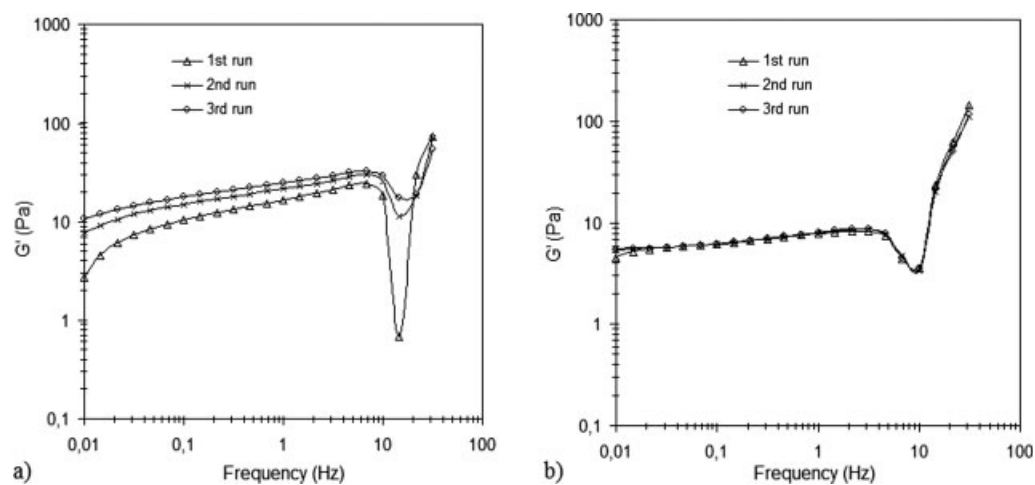


Figure 12 Results of three consecutive frequency sweeps for (a) emulsion-based plastisol and (b) microsuspension-based plastisol.

resin. The results show that the emulsion-based plastisol is much more prone to ageing than the microsuspension-based one, probably because of the higher rigidity and lower permeability to plasticizer action of the latter.

The results also showed that for the emulsion plastisol both the viscosity and the apparent yield stress increase significantly with time, while the microsuspension plastisol keeps the same viscosity, apparent yield stress, and gelation behavior over the entire month. The gelation kinetic remains unaltered for both plastisols over time, but the onset of gelation increase with ageing in the emulsion plastisol while it remains constant in the case of the microsuspension one.

Concerning the oscillatory shear tests, the results showed again that, unlike the emulsion-based plasti-

sol, the microsuspension one is very stable in time. Furthermore, an unexpected behavior in the storage modulus was observed for both plastisols: there was a frequency range within which there was drop in the storage modulus, i.e., the elastic response, but not in the loss modulus, i.e., the viscous response. After discarding the possibility of experimental error, the most likely explanation for this effect is that it is due to plasticizer adsorption onto the surface of the PVC particles, i.e., the beginning of the ageing process. This effect was completely reversible for the microsuspension-based plastisol but not for emulsion-based one, which agrees well with the ageing behavior of both fluids and provides an extra quick test of the susceptibility to ageing of plastisols and/or to differentiate between resin types in different plastisols.

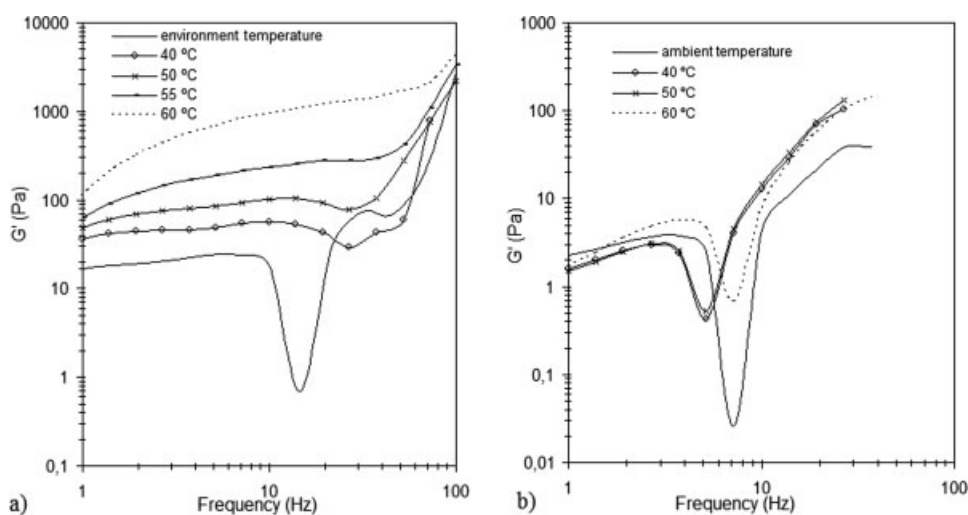


Figure 13 Influence of temperature on the depression in G' for (a) emulsion-based plastisol and (b) microsuspension-based plastisol.

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