PII: S0032-3861(97)00297-8

*Polymer* Vol. 39 No. 2, pp. 431–435, 1998

0032-3861/97/$17.00+0.00

# Influence of the type of resin in the gelation and fusion processes of PVC plastisols

**J. C. García* and A. Marcilla**
*Departamento de Ingeniería Química, Universidad de Alicante, 03080, Alicante, Apartado 99, España*
*(Received 2 December 1996; revised 23 January 1997)*

A rheological study of the influence of the type of resin in the gelation and fusion processes of PVC plastisols was carried out using several commercial PVC resins, with different particle size distribution and molecular weight. Results obtained prove that the gelation rate and the moduli developed increase with decreasing both the particle size and molecular weight. © 1997 Elsevier Science Ltd.

**(Keywords: gelation; fusion; plastisol)**

## INTRODUCTION

PVC plastisols are suspensions consisting of particles of a PVC resin in a liquid continuous phase, formed mainly by a plasticizer and a stabilizer. Normally the PVC resin obtained by the emulsion or microsuspension methods is used, though sometimes they can be partly substituted by suspension or mass resins.

Emulsion and microsuspension resins are made up of two kinds of particles: i.e. primary particles, with an average diameter of about 1 $\mu$m and secondary particles, which are the result of the agglomeration of the primary particles, with sizes up to 45 $\mu$m. If the polyerisation process has been run under severe conditions, the secondary particles are very difficult to break. However, if the polymerisation conditions have been mild, secondary particles are broken easily and can be broken during the mixing process in the plastisol preparation. In previous research[1] a relationship between the rheological behaviour of the plastisols and the amount of the primary particles was observed.

When a plastisol is heated up to 180–200°C it undergoes two processes, known as gelation and fusion. In the first, the PVC resin is dissolved in the continuous phase, yielding a gel, where some researchers have pointed out the existence of PVC microcrystallites which form a network structure responsible for its properties[2–4]. In the second process (fusion), the network structure is destroyed by fusion of the microcrystallites, reaching a homogeneous state, which in a further cooling step leads to a solid polymer with all the properties of the plasticised PVC.

One of the most useful methods to monitor the gelation and fusion processes is the characterisation of the system by viscoelastic measurements in oscillatory test. This widely used[5–13] method analyses the variation of the rheological properties of the plastisol with the temperature. As a result of this type of experiment the following trends have been described: Initially, when the temperature increases, a decrease in the viscosity is observed. The system behaves as a suspension of non interacting PVC particles in the plasticizer, which constitutes the continuous phase, whose viscosity decreases with temperature. In a later stage, the gelation begins producing a marked increase in both the moduli and the viscosity, both of which reach a plateau or a maximum. PVC particles start to swell and interact among themselves developing a gel structure with poor mechanical strength. At the end of the gelation, a further increase in temperature produces a viscosity decrease, probably due to both reasons: the thermal expansion and the fusion process[2].

The objective of the present work is to study the effect of some commercial resins with different properties in the rheology of their plastisols during the gelation and fusion processes.

## EXPERIMENTAL

64 phr of the Jayflex DOP (di-2-ethylhexyl phtalate) plasticizer, from EXXON and 6.4 phr of the calcium–zinc stabilizer ASUA 656 T 2 from Industria Químicas ASUA (Bilbao, SPAIN), were employed in all plastisol formulations.

Several standard commercial resins in plastisol applications were used. Resins employed can be classified into two groups:

a) Resins obtained by the emulsion process. ETINOX 450 from AISCONDEL and HISPAVIC 367 A, HISPAVIC 367 B (corresponding to different years) from SOLVAY.
b) Resins obtained by the miscrosuspension process, supplied by RÍO RODANO. These resins are MIRVYL 1172, MIRVYL 1302 and MIRVYL 1702.

Particle size distribution and molecular weight were determined to characterise the resins.

### *Molecular weight*

The molecular weights of the different resins employed were determined by Gel Permeation Chromatography (GPC) in THF; using a differential refractometer/viscometer VISCOTEK model 200 with a 7.8 mm inner diameter and 30 cm. long TSK gel column G4000HXL. All the samples were diluted to approximately 1.5 mg of PVC per ml of THF. The injection volume was 0.1 ml and a flow rate of

---

* To whom correspondence should be addressed

**Table 1** Molecular weights and $K$ values of the resins employed and fraction of particles of the distribution with a size lower than 1.25 $\mu$m

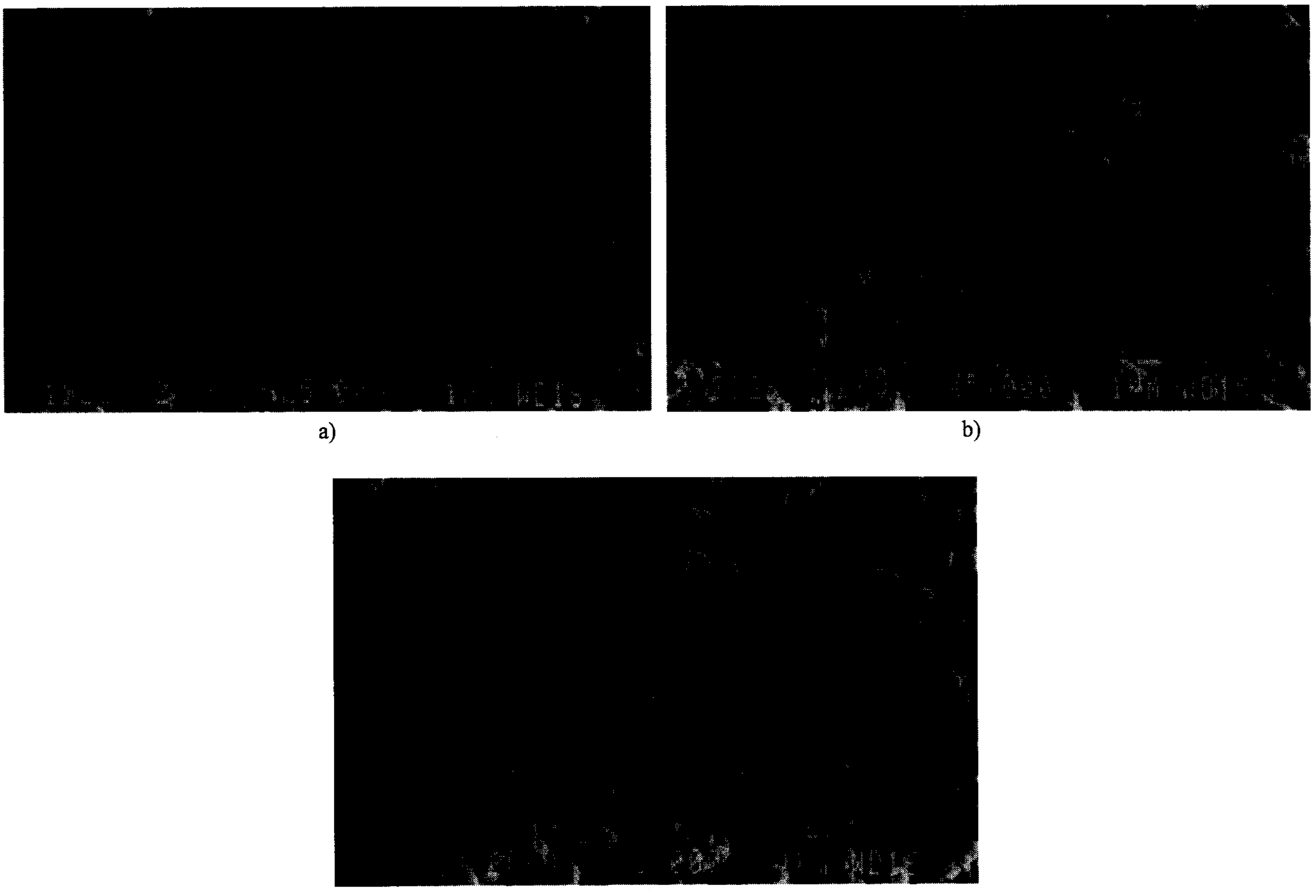
| Resin | $M_w$ | Polidispersity ($M_w/M_z$) | Intrinsic Viscosity (dl/g) | $K$ | Fraction under 1.25$\mu$m(%) |
|---|---|---|---|---|---|
| ETINOX 450 | 101600 | 3.090 | 1.440 | 67 | 24 |
| HISPAVIC 367 A | 101300 | 3.060 | 1.387 | 67 | 79 |
| HISPAVIC 367 B | – | – | – | 67 | 38 |
| MIRVYL 1172 | 101900 | 2.717 | 1.358 | 68 | 67 |
| MIRVYL 1302 | 110300 | 2.819 | 1.638 | 71 | 62 |
| MIRVYL 1702 | 144400 | 2.927 | 2.065 | 80 | 60 |

1.0 ml of THF/min as eluent was used. On the other hand, the $K$-value of each resin was known from the supplier. The $K$-value and the data obtained by GPC are shown in *Table 1.*

### *Particle size distribution*

In previous studies[1,14] particle size distribution of the resin was determined by laser diffraction and gravitational sedimentation; however, these methods have the disadvantage that it is not possible to observe significant differences in the primary particle size distribution of the different resins. For this reason, we have applied a method similar to that reported by Mahmud et al.[15] for determining the particle size distribution of resins obtained by the suspension method. In this way, the different resins were observed by scanning electronic microscopy (SEM) using a JEOL 840 JSM microscope; images taken for all resins can be observed in *Figures 1 and 2* (as examples); they were used to count every fraction of particles between two given particle sizes, allowing an estimation of the primary particle size distribution. Particle size distribution of the resins can be observed in *Figure 3* and *Figure 4*. Moreover, in order to have a parameter related to the particle size distribution of each resin, the fraction of particles under 1.25 $\mu$m has also been included in *Table 1.*

Gelation and fusion were studied by analysing the viscoelastic properties in a rheometer BOHLIN CS 50, in oscillatory tests between 40°C and 180°C with a heating rate of 10°C/min. The influence of the different conditions of measurement which affect the viscoelastic properties were studied previously[1]; 20 mm diameter parallel plates with a GAP of 0.7 mm were used. In all cases, the deformation amplitude was low enough (0.005) to apply the linear viscoelasticity equations. The oscillation frequency was 1 Hz.


a)

b)

c)

**Figure 1** Aspect of the resins a) ETINOX 450, b) HISPAVIC 367 A and c) HISPAVIC 367 B at 5000 magnifications

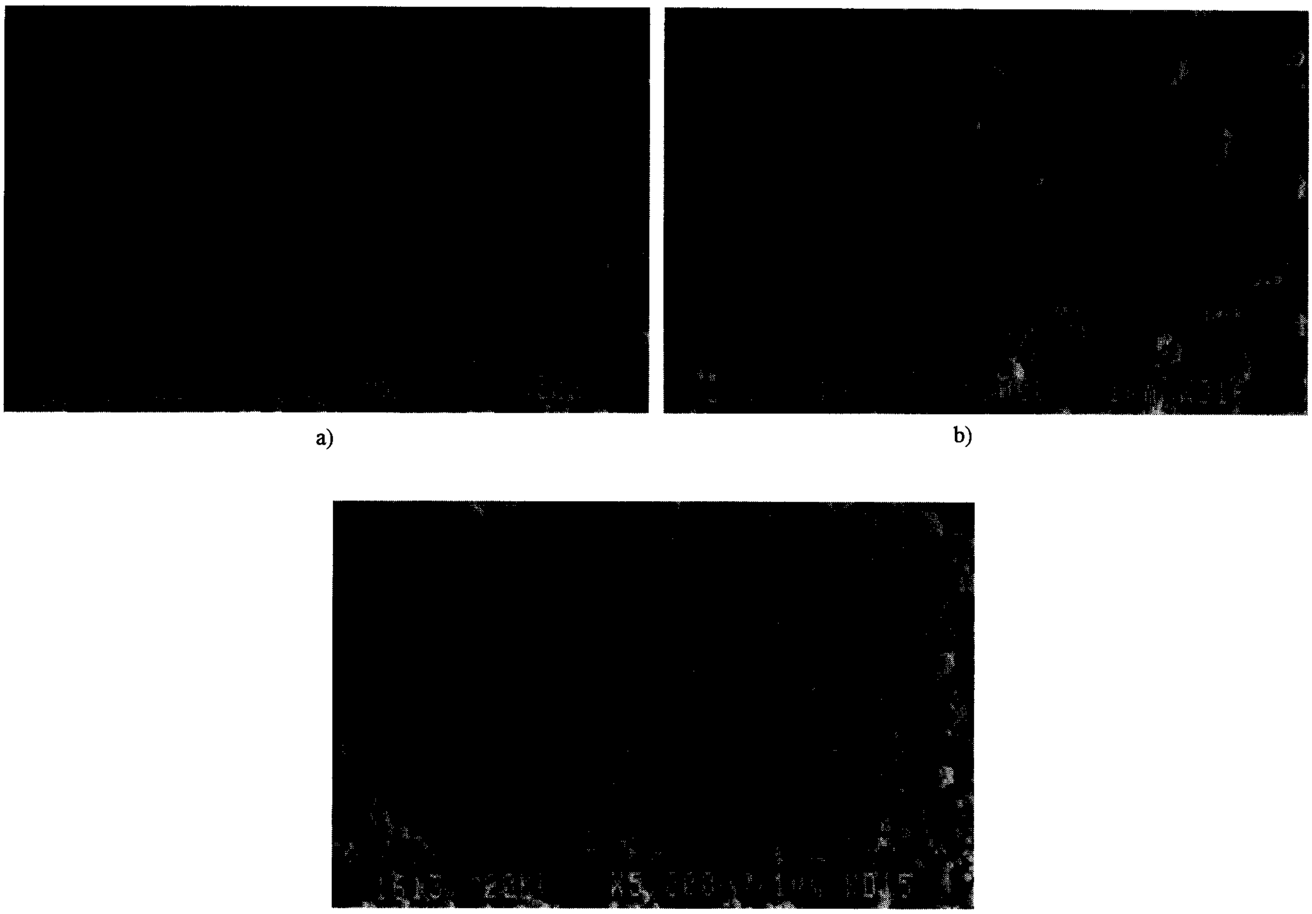


**Figure 2** Aspect of the resins a) MIRVYL 1172, b) MIRVYL 1302 and c) MIRVYL 1702 at 5000 magnifications

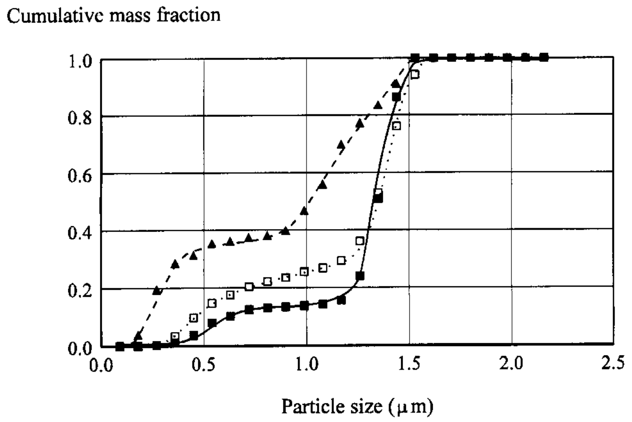


**Figure 3** Particle size distribution of the resins: ■, ETINOX 450 ▲, HISPAVIC 367 A and □, HISPAVIC 367 B

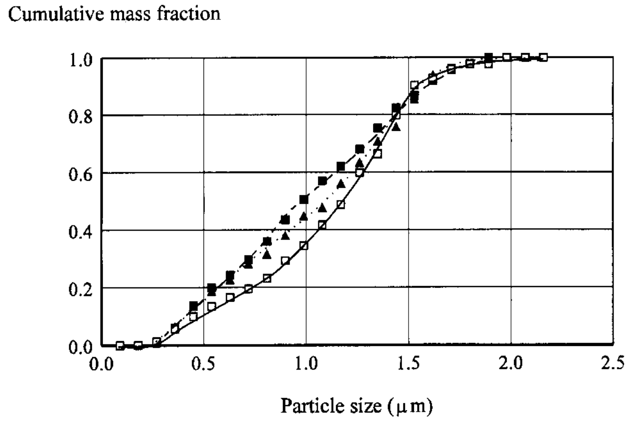


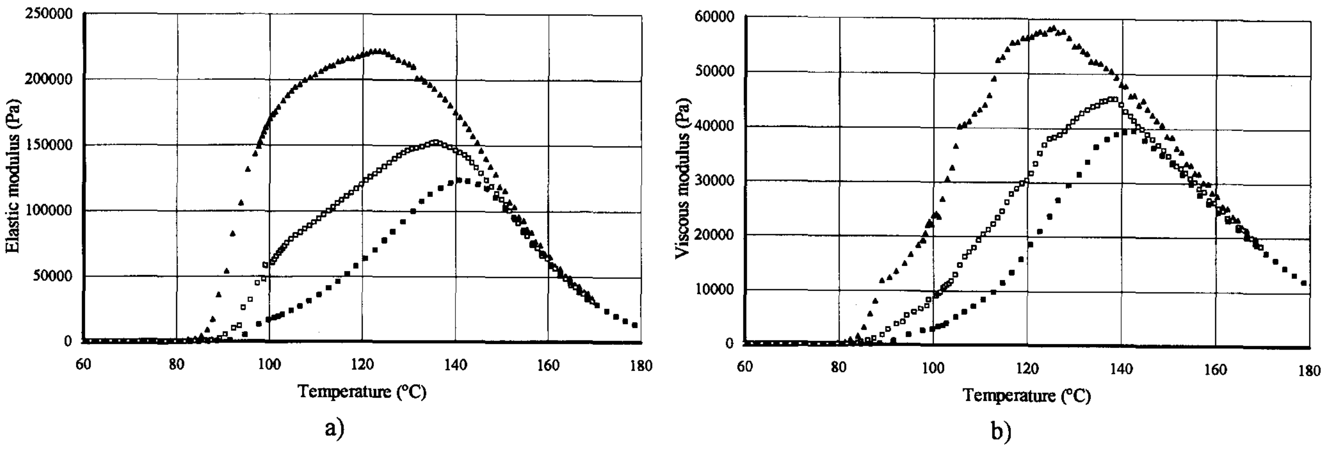
**Figure 4** Particle size distribution of the resins: ■, MIRVYL 1172 ▲, MIRVYL 1302 and □, MIRVYL 1702

## RESULTS

Resins employed allow the influence of particle size distribution to be studied, since the resins ETINOX 450, HISPAVIC 367 A and HISPAVIC 367 B the molecular weight (or *K*-values) are very close, though with different particle size distribution. On the other hand, they also allow the influence of molecular weight to be studied, since MIRVYL resins have a very similar particle size distribution but different molecular weight (or *K*-value).

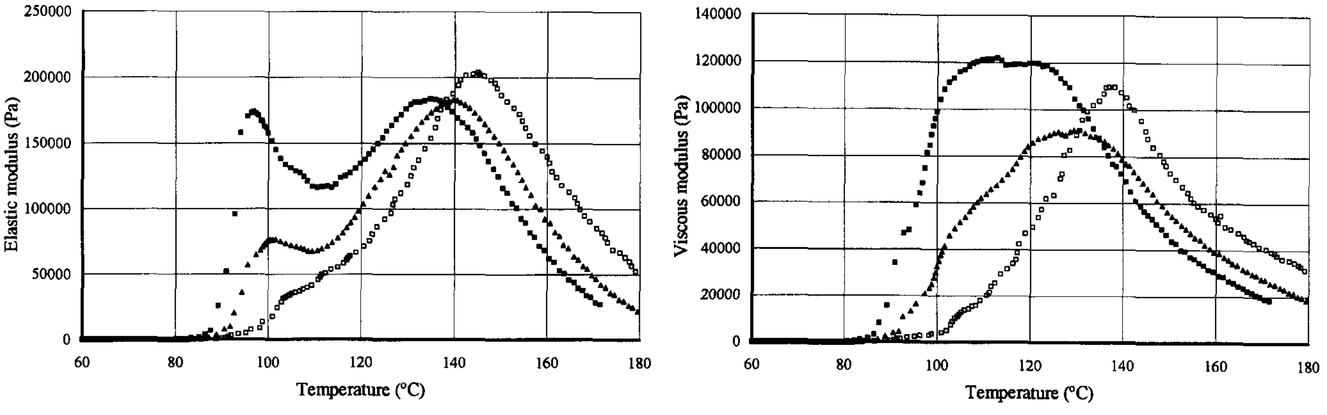
In this way, the influence of molecular weight and particle size distribution in rheological properties (elastic and viscous modulus) were studied.

It is necessary to bear in mind that all resins are commercial PVC resins and besides the molecular weight and the particle size distribution there are other factors (i.e. different type or concentration of additives coming from the polymerisation process, porosity, ...) which could cause deviations from the expected behaviour if only molecular weight and particle size distribution are considered. An important factor to consider is the presence of the polymerisation additives (e.g. emulsifiers) which can affect the measurements. However, valuable conclusions with regard to the influence of the particle size and molecular weight can be drawn by comparing plastisols



a) b)

**Figure 5** Behaviour of (a) elastic modulus and (b) viscous modulus for plastisols with: ■, ETINOX 450 ▲, HISPAVIC 367 A and □, HISPAVIC 367 B



a) b)

**Figure 6** Behaviour of (a) elastic modulus and (b) viscous modulus for plastisols with: ■, MIRVYL 1172 ▲, MIRVYL 1302 and □, MIRVYL 1702

made up from resins obtained by the same polymerisation process. On comparing results from emulsion resins at temperatures above 150°C (i.e. when fusion process dominates) all resins have the same modulus due to their similar molecular weight, and no effect either due to differences in particle size distribution or possible differences in the type of concentration of additives has been observed.

## INFLUENCE OF THE PARTICLE SIZE DISTRIBUTION

In order to study the influence of the particle size distribution of the resins, plastisols with resins ETINOX 450, HISPAVIC 367 A and HISPAVIC 367 B were compared. Elastic and viscous moduli of the plastisols made with these resins are shown in *Figure 5*. It can be observed that both the elastic and viscous moduli of the plastisols follow similar trends, though the shape of the curves are somewhat different.

It is worth noting that the order observed in the rate of the gelation process is the same as the order of the resins according to their smaller particle content, i.e.:

$$\begin{array}{ccccc} \text{HISPAVIC 367 A} & & \text{HISPAVIC 367 B} & & \text{ETINOX 450} \\ (F_{1.25}=79\%) & > & (F_{1.25}=38\%) & > & (F_{1.25}=24\%) \end{array}$$

This fact can be explained on considering that the smaller particle size favours the interactions between the resin and the plasticizer$^2$, causing the plastisols from the resins with smaller particles to gel faster.

On the other hand, and as a consequence of the fast interaction between the resin and the plasticizer, the moduli of the plastisols whose resins have the smallest particles are higher. For example at 100°C:

$$\begin{array}{ccccc} \text{HISPAVIC 367 A} & & \text{HISPAVIC 367 B} & & \text{ETINOX 450} \\ \begin{pmatrix} G' = 1.71\ 10^5\ \text{Pa} \\ G'' = 2.39\ 10^4\ \text{Pa} \end{pmatrix} & > & \begin{pmatrix} G' = 6.07\ 10^4\ \text{Pa} \\ G'' = 9.10\ 10^3\ \text{Pa} \end{pmatrix} & > & \begin{pmatrix} G' = 1.65\ 10^4\ \text{Pa} \\ G'' = 2.98\ 10^3\ \text{Pa} \end{pmatrix} \end{array}$$

However, at higher temperatrures when fusion has started (approximately around 150°C) the elastic and viscous moduli of all plastisols are very similar, indicating that at this point the structure of the suspension has disappeared and the molecular weight of the gel obtained (i.e. the average molecular weight calculated according to the mass fraction in the plastisol and the molecular weights of the resin, the plasticizer and the stabilizer) determines the behaviour of both moduli.

## INFLUENCE OF THE MOLECULAR WEIGHT

The elastic modulus and viscous modulus obtained in the oscillatory tests from plastisols with the PVC resins MIRVYL 1172, MIRVYL 1302 and MIRVYL 1702 are shown in *Figure 6*.

It is important to observe the different behaviour between elastic and viscous moduli. The viscous modulus shows a progressive increase until a given temperature, where fusion has already started. At higher temperatures, the viscous modulus decreases. However, the elastic modulus of plastisols with MIRVYL 1172 and MIRVYL 1302 has a more complex behaviour, since it presents two maxima, which can be due to the presence of parts of the resin that gel faster than others (probably those with smaller particles or lower molecular weight), in agreement with the results obtained by Nakajima et al.[8] in plastisols with other commercial resins.

Another fact which must be mentioned is that the rate of gelation observed decreases with the molecular weight of the resins, as observed by other authors[10,13]:

$$\begin{array}{ccccc} \text{MIRVYL 1172} & & \text{MIRVYL 1302} & & \text{MIRVYL 1702} \\ (M_w = 101900) & > & (M_w = 110300) & > & (M_w = 144400) \end{array}$$

On the other hand, when gelation has started, the moduli of plastisols with resins of lower molecular weight reach the higher values, probably as a consequence of the stronger interactions established between the plasticizer and the resin in such cases. However, a maxima in the viscous modulus curves do not follow a clear trend. Difference in the type or concentration of polymerisation additives may explain this behaviour.

Nevertheless, at temperatures where the fusion process has notably progressed, the order observed from both moduli is the same as that corresponding to the molecular weight of the resin employed. For example at 170°C, the elastic and viscous moduli of plastisols with the different resins are the following:

$$\begin{array}{ccccc} \text{MIRVYL 1171} & & \text{MIRVYL 1302} & & \text{MIRVYL 1702} \\ \begin{pmatrix} G' = 2.86\ 10^4\ \text{Pa} \\ G'' = 1.39\ 10^4\ \text{Pa} \\ M_w = 101900 \end{pmatrix} & < & \begin{pmatrix} G' = 3.77\ 10^4\ \text{Pa} \\ G'' = 2.38\ 10^4\ \text{Pa} \\ M_w = 110300 \end{pmatrix} & < & \begin{pmatrix} G' = 8.58\ 10^4\ \text{Pa} \\ G'' = 4.15\ 10^4\ \text{Pa} \\ M_w = 144400 \end{pmatrix} \end{array}$$

## CONCLUSIONS

The following conclusions can be obtained in the present study:

(1) Scanning electronic microscopy is a reliable technique, very useful for the determination of particle size distribution of the PVC resins. Results obtained with this method allow a better correlation between particle size distribution and the behaviour observed during the gelation and fusion processes than other methods such as sedimentation gravitational or laser diffraction, which cannot adequately determine the particle size distribution in the range size of these kinds of resins with fine particles.

(2) With respect to the rheological study:

a) Plastisols from resins with larger fractions of fine particles gel faster and reach higher moduli in the gelation temperature range than plastisols from resins with larger particles. Different characteristics such as the type or concentration of polymerisation additives may explain deviations from the expected behaviour of plastisols from resins obtained by different polymerisation processes.

b) Plastisols from resins with the same particle size distribution and lower molecular weight gel faster than plastisols from resins with higher molecular weight.

c) The moduli and complex viscosity of plastisols in the fusion range is strongly dependent on molecular weight of the PVC.

## ACKNOWLEDGEMENTS

The authors of the paper wish to thank the Conselleria de Educació i Ciència de la Generalitat Valenciana and FAMOSA (Fábricas Asociadas de Muñecas de Onil S.A.).

## REFERENCES

1. Marcilla, A., and Garcia, J. C., *Eur. Polym. J.*, 1997, **33**, 49.
2. Nakajima, N. and Harrell, E. R., *Adv. Polym. Technol.*, 1986, **6**, 409.
3. Nijenius, K. T. and Winter, H. H., *Macromol.*, 1989, **22**, 411.
4. Gallego, F., Munoz, M. E., Pena, J. J. and Santamaria, A., *Eur. Polym. J.*, 1988, **24**, 327.
5. Nakajima, N., Ward, D. W. and Collins, E. A., *J. Appl. Polym. Sci.*, 1976, **20**, 1187.
6. Nakajima, N., Ward, D. W. and Collins, E. A., *Polym. Eng. and Sci.*, 1979, **19**, 210.
7. Nakajima, N. and Daniels, C. A., *J. Appl. Polym. Sci.*, 1980, **25**, 2019.
8. Nakajima, N. and Ward, D., *Rubber Chem. and Technol.*, 1981, **54**, 1096.
9. Nakajima, N., Isner, J. D., Harrell, E. R. and Daniels, C. A., *Polym. J.*, 1981, **13**, 955.
10. Nakajima, N. and Ward, D. W., *J. Appl. Polym. Sci.*, 1983, **28**, 807.
11. Nakajima, N. and Sadeghi, M. R., *Intern. Polym. Process. IV*, 1989, **1**, 16.
12. Nakajima, N. and Kwak, S. Y., *J. Vinyl Technol.*, 1991, **13**, 212.
13. Guoquan, W. and Yiaotin, C., *Polymer Testing*, 1991, **10**, 315.
14. Marcilla, A., Garcia, J. C., and Beltrán, M., *Eur. Polym. J.*, 1997, **33**, 753.
15. Mahmud, F., Atiqullah, M., Jarrah, N. and Hussain, I., *Eur. Polym. J.*, 1992, **28**, 1039.