Polymer Vol. 39 No. 15, pp. 3507–3514, 1998
© 1998 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

PII: S0032-3861(97)10033-7

Rheological study of the influence of the plasticizer concentration 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, Spain
(Received 23 December 1996; revised 5 June 1997)

The influence of the type of plasticizer and its concentration on the rheological behaviour of plastisols made from several commercial resins during the gelation and fusion processes has been studied. The use of different concentrations of plasticizers as well as plasticizers with different compatibilities has allowed the observation of relevant differences in the behaviour of the elastic and viscous moduli in plastisols with low concentration of plasticizer as well as in plastisols prepared with plasticizers having higher compatibility with PVC. In addition, scanning electron microscopy has been used in order to obtain a better understanding of the gelation and fusion processes. © 1998 Elsevier Science Ltd. All rights reserved.

(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. All the industrial processes for plastisols involve the heating of the plastisol in an oven at about 180–200°C, where the plastisol undergoes two processes known as gelation and fusion.

One of the most useful methods of monitoring gelation and fusion is viscoelastic characterization by means of oscillation tests, as previously stated[1–12]. The most frequently used parameters are the elastic (G') and the viscous moduli (G''), although complex viscosity (η^*) and loss tangent (tg δ) can also be employed in the study of both processes. Generally, during these kinds of experiment the following trends can be observed from both moduli and the complex viscosity. Initially, when the temperature increases, a decrease takes place in the moduli and in the viscosity. The system behaves as a suspension of non-interacting PVC particles in the plasticizer, which constitutes the continuous phase whose viscosity decreases with temperature. At a later stage, gelation begins to produce a marked increase in both moduli and viscosity, due to the swelling of the PVC particles and the interaction among themselves which develops a gel structure with poor mechanical strength, reaching at this point a plateau or maximum of the moduli and viscosity. In some cases, depending on the type of resin and its concentration, the gelation process can occur in two different steps, probably due to the gelation of zones of the resin which interact with the plasticizer at a different speed[1,2]. At the end of gelation, a further increase in temperature produces a viscosity decrease, probably due to two reasons: thermal expansion and the fusion process.

However, the temperature at which both processes (i.e. gelation and fusion) appear and the magnitude of the changes observed are strongly dependent on two types of parameter to be considered: the measurement conditions and the formulation used. On the one hand measurement conditions[3], such as oscillation frequency, heating rate[4] or deformation amplitude, can notably affect the evolution observed in both moduli. On the other hand, the formulation used is the most interesting factor to bear in mind, since both the type of resin[1,2,5–8] and of plasticizers[9,10] and their concentration strongly affect the gelation and fusion and therefore the observed behaviour of the moduli. As already poionted out, an increase in the particle size and in the molecular weight[7] of the resin causes both processes to appear at higher temperatures, and the changes observed are more uniform. With respect to the concentration of plasticizer, it has already been observed in previous studies[11] that moduli reached during gelation and fusion are lower when the plasticizer concentration is increased, and the changes are less marked. However, the use of low concentrations of plasticizer reveals greater differences in the way that both moduli are affected by the gelation[11].

Finally, SEM (scanning electron microscopy) has been used in previous works[7,8,12,13] in order to study gelation and fusion of PVC plastisols from different PVC resins and different plasticizers, showing that this is a reliable technique for studying gelation and fusion of PVC plastisols. In the present work, SEM has been employed together with viscoelastic measurements to study the gelation and fusion processes of different plastisols from different commercial resins and with different concentrations of several plasticizers with differing solvent power in order to obtain a better understanding of the effect of these parameters on the behaviour of both moduli.

EXPERIMENTAL

The plasticizers Jayflex DOP (di-2-ethylhexyl phthalate), Jayflex DIDP (di-isodecyl phthalate) from Exxon, Palatinol

---

*To whom correspondence should be addressed

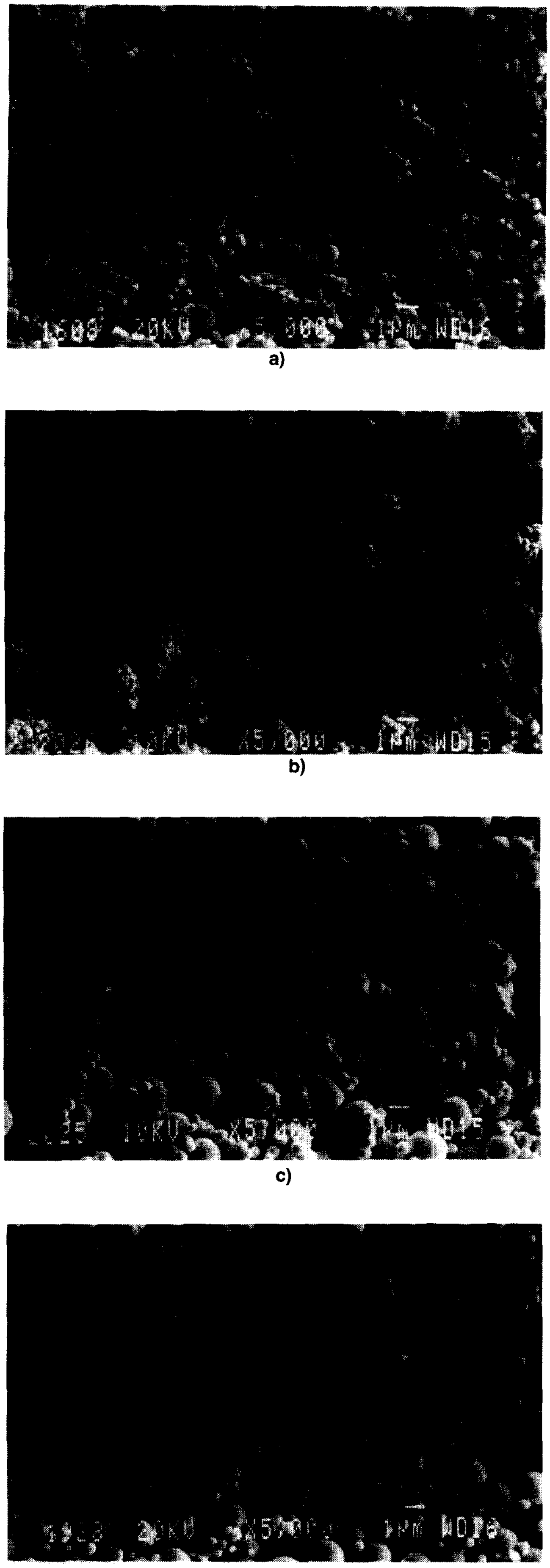


Figure 1 Appearance of the PVC resins: (a) MIRVYL 1172; (b) HISPAVIC 367; (c) ETINOX 440; (d) ETINOX 450

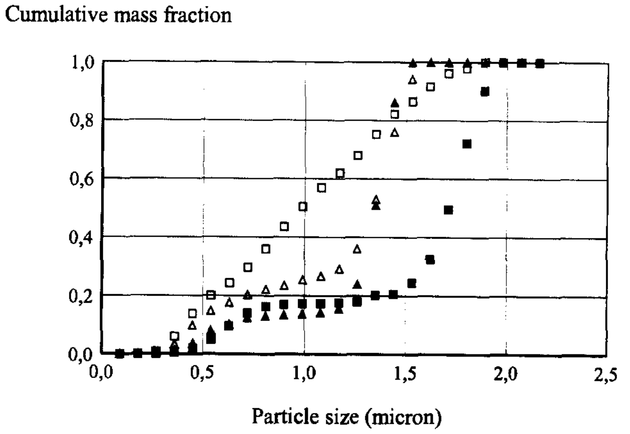


Figure 2 Primary particle size distribution of the PVC resins: □ MIRVYL 1172; △ HISPAVIC 367; ■ ETINOX 440; ▲ ETINOX 450

Table 1 Data related to the molecular weight of the resins employed

Resin	M_w	Polydispersity (M_w/M_n)	Intrinsic viscosity (dl g^{-1})	K
MIRVYL 1172 (microsuspension resin)	101 900	2.72	1.36	68
HISPAVIC 367 (emulsion resin)	101 300	3.06	1.39	67
ETINOX 440 (emulsion resin)	121 100	3.09	1.69	75
ETINOX 450 (emulsion resin)	101 600	3.04	1.44	67

DINP (di-isononyl phthalate) from BASF and the calcium–zinc stabilizer ASUA 656 T 2 from Industrias Químicas ASUA (Bilbao, Spain) were employed.

Standard commercial PVC resins in plastisol applications, MIRVYL 1172 from Río Ródano, HISPAVIC 367 from Solvay and ETINOX 440 and ETINOX 450 from Aiscondel were used.

In order to characterise the particle size of the resins, these were observed by scanning electron microscopy; the appearance of the PVC resins at magnification 5000 is shown in *Figure 1*. This figure has been used to determine the primary particle size distribution of the resins, as reported elsewhere[2]. The particle size distribution of the resins is shown in *Figure 2*.

The molecular weights of the resins were determined by gel peremeation chromatography (g.p.c.) in THF (tetrahydrofuran), using a differential refractometer/ viscometer Viscotek model 200, with a 7.8 mm inner diameter and 30 cm long TSK gel column G4000HXL. Samples were diluted to approximatley 1.5 mg of PVC per ml of THF. The injection volume was 0.1 ml and a flow rate of 1.0 ml of THF min^{-1} as eluent was used; data obtained are shown in *Table 1* together with the *K* value provided by the supplier.

In summary, the resins chosen for this study have the following characteristics (from *Table 1* and *Figure 2*):

- Resin MIRVYL 1172: Microsuspension resin with average molecular weight (101 900) and a wide primary particle size distribution.
- Resin HISPAVIC 367: Emulsion resin with average molecular weight (101 300) and a bimodal primary particle size distribution, but with a higher fraction of the

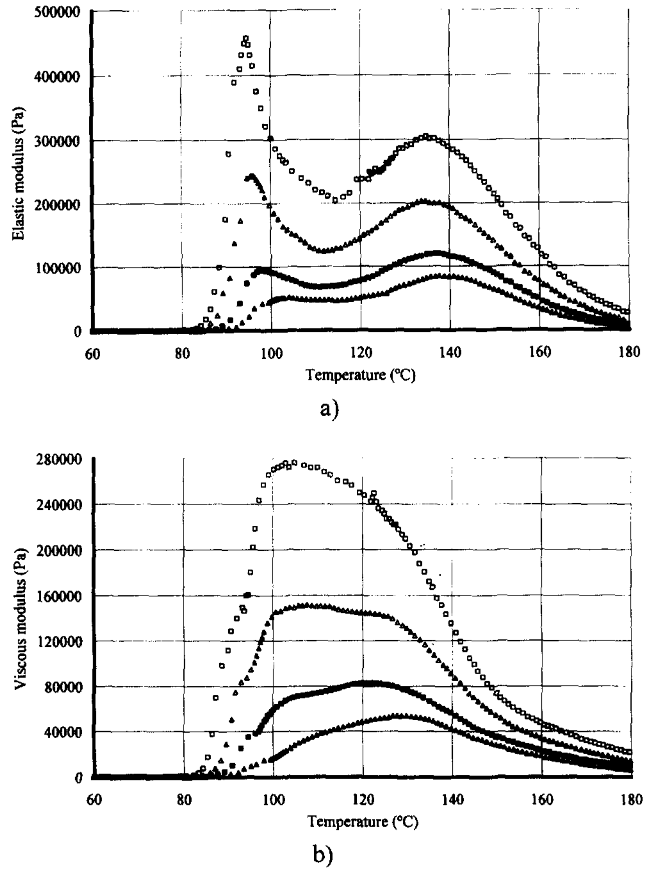


Figure 3 Behaviour of the elastic and viscous moduli for plastisols with MIRVYL 1172 and DOP: △ 50 phr; ○ 60 phr; ■ 70 phr; ▲ 80 phr

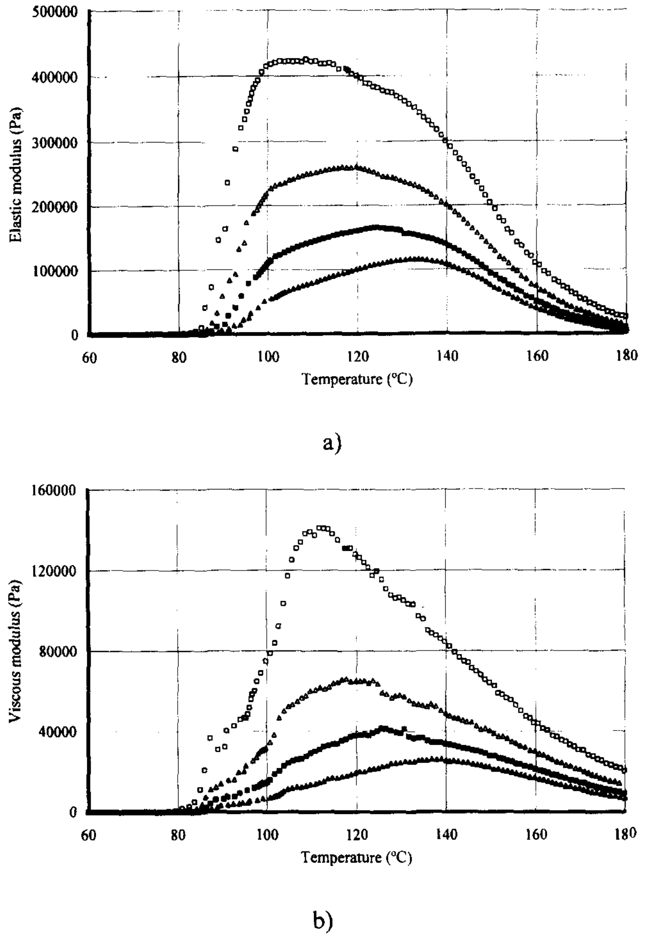


Figure 4 Behaviour of the elastic and viscous moduli for plastisols with HISPAVIC 367 and DOP: △ 50 phr; ○ 60 phr; ■ 70 phr; ▲ 80 phr

smallest particles (i.e. those smaller than ~1.25 μm) than the other resins.

- Resin ETINOX 440: Emulsion resin with high molecular weight (121 000) and bimodal primary particle size distribution, with particles of higher size than the other resins.
- Resin ETINOX 450: Emulsion resin with average molecular weight (101 600) similar to that of HISPAVIC 367, with a bimodal particle size distribution but with a lower fraction of the smallest particles than HISPAVIC 367.

Plastisols were prepared from the respective resins and different concentrations of DOP, DINP and DIDP, all with 6.4 phr of stabilizer.

Plastisols were heated in a rheometer, Bohlin CS 50, in oscillatory tests between 40°C to 180°C at a heating rate of 10°C min^{-1}. The measurement system employed was that of 20 mm diameter parallel plates with a gap of 0.7 mm. The deformation amplitude was 0.005 and the oscillation frequency 1 Hz.

RESULTS

Results obtained during the oscillation tests for plastisols with the resins MIRVYL 1172, HISPAVIC 367, ETINOX 440 and ETINOX 450 and different concentrations of DOP are shown in *Figures 3–6*.

During the gelation process an increase in moduli is observed, associated with the dissolution of the PVC particles in the continuous phase of the plastisol (which initially consists mainly of the plasticizer), up to a temperature where the gelation process concludes and the thermal expansion and the fusion process cause a decrease in both moduli. The increase in moduli is parallel to the dissolution of the PVC particles; for example, the evolution of the morphology with temperature for plastisols with the resins ETINOX 450 and MIRVYL 1172 can be observed in *Figures 7 and 8*. At temperatures where gelation has already started, for example 110°C (*Figure 7a* to *Figure 8a*), it is possible to observe that some particles, especially those of low particle size (i.e. smaller than ~1 μm), which were initially in the resin, have already disappeared; instead, a continuous phase joining the ungelled particles can be observed, the fraction of the continuous phase being higher in the MIRVYL 1172 plastisol. This indicates that the gelation process in this case has reached a more advanced state, in good agreement with the viscoelastic measurements, since the increases in modulus in these plastisols occur at lower temperatures (*Figure 3a* to *Figure 6a*). At higher temperatures (140°C) in both plastisols (*Figure 7b* to *Figure 8b*) it is possible to observe that the fraction of continuous phase present in the plastisol has increased and that the size and number of ungelled particles are lower, showing a more advanced state in the gelation process, which almost stops at 160°C (*Figure 7c* to *Figure 8c*), making it possible only to observe certain irregularities in the surface which may constitute the last portions of the PVC resin to gel.

Figures 3 and 4 do not include the data corresponding to the plastisol with 45 phr of DOP since the moduli reached

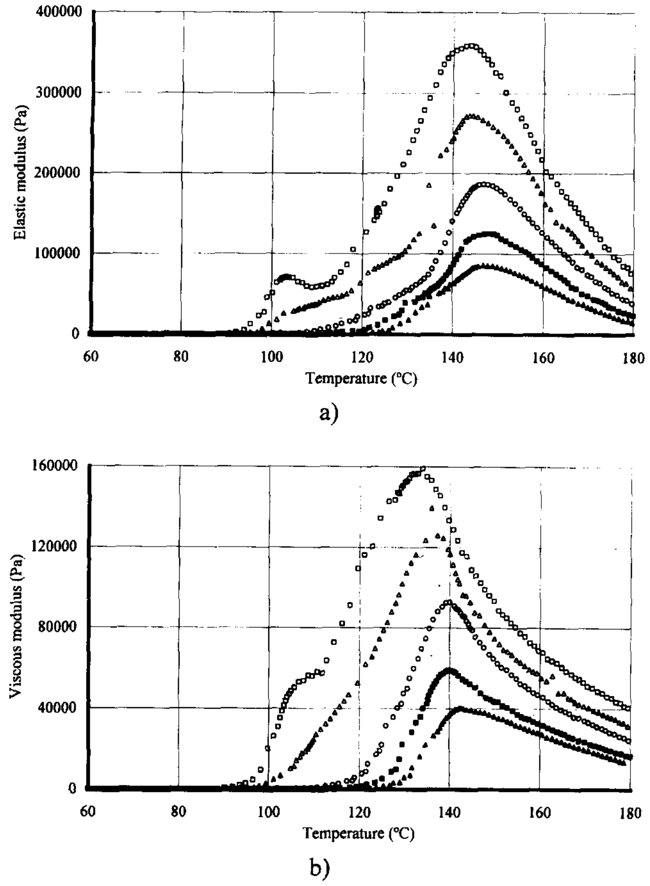


Figure 5 Behaviour of the elastic and viscous moduli for plastisols with ETINOX 440 and DOP: □ 45 phr; △ 50 phr; ○ 60 phr; ■ 70 phr ▲ 80 phr

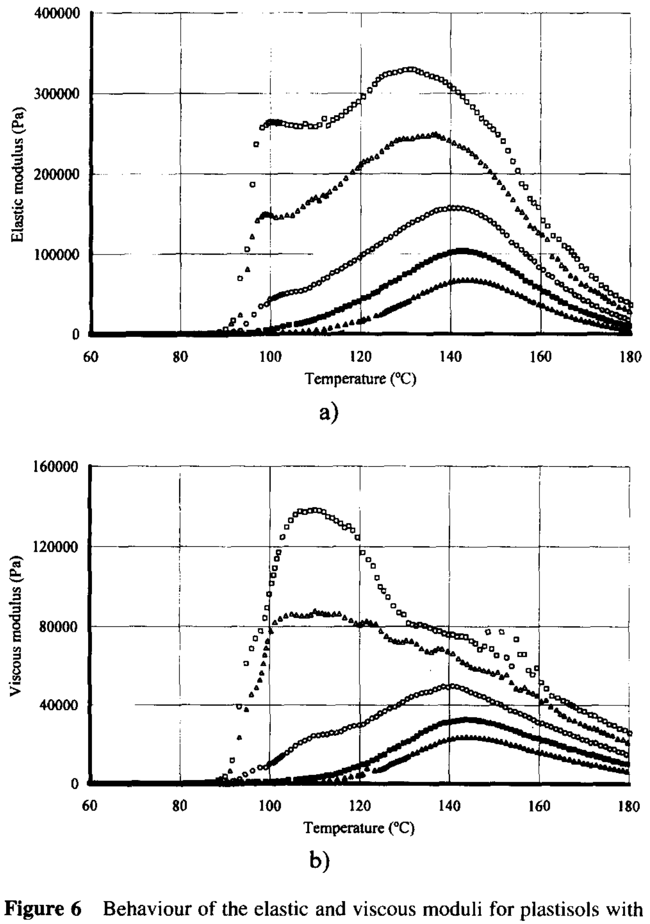


Figure 6 Behaviour of the elastic and viscous moduli for plastisols with ETINOX 450 and DOP: □ 45 phr; △ 50 phr; ○ 60 phr; ■ 70 phr; ▲ 80 phr

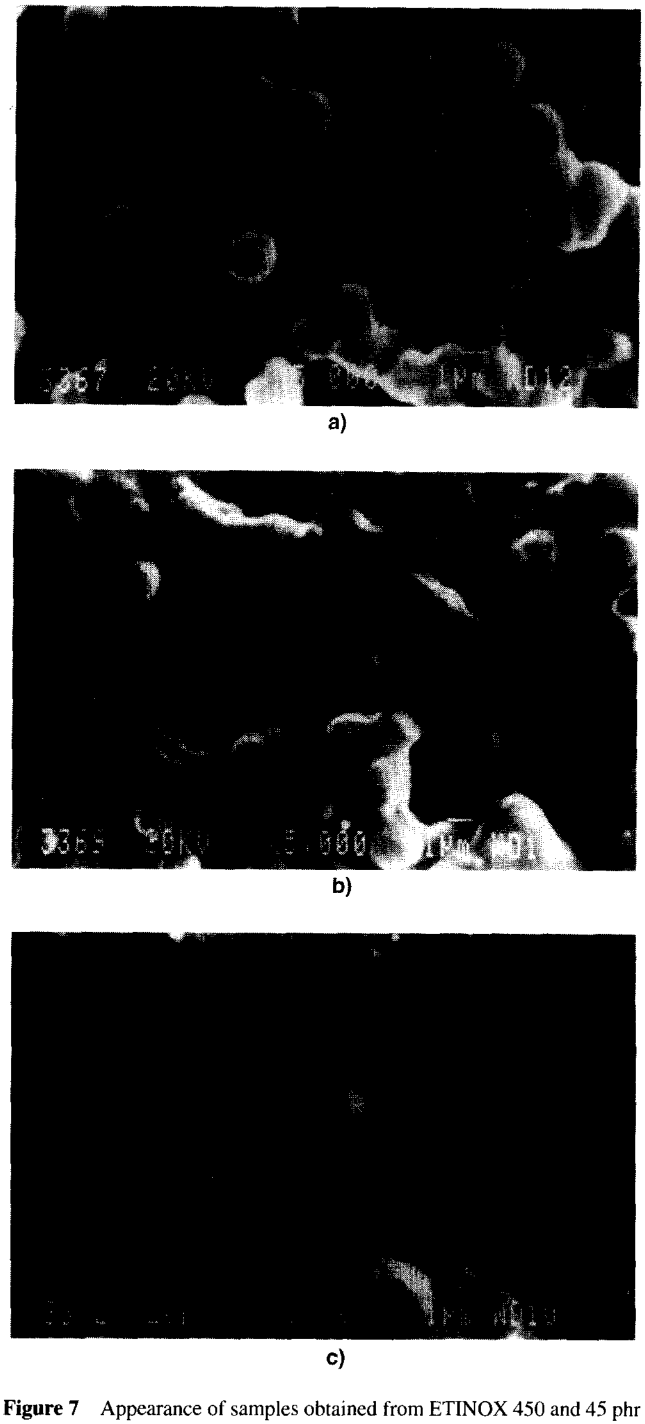
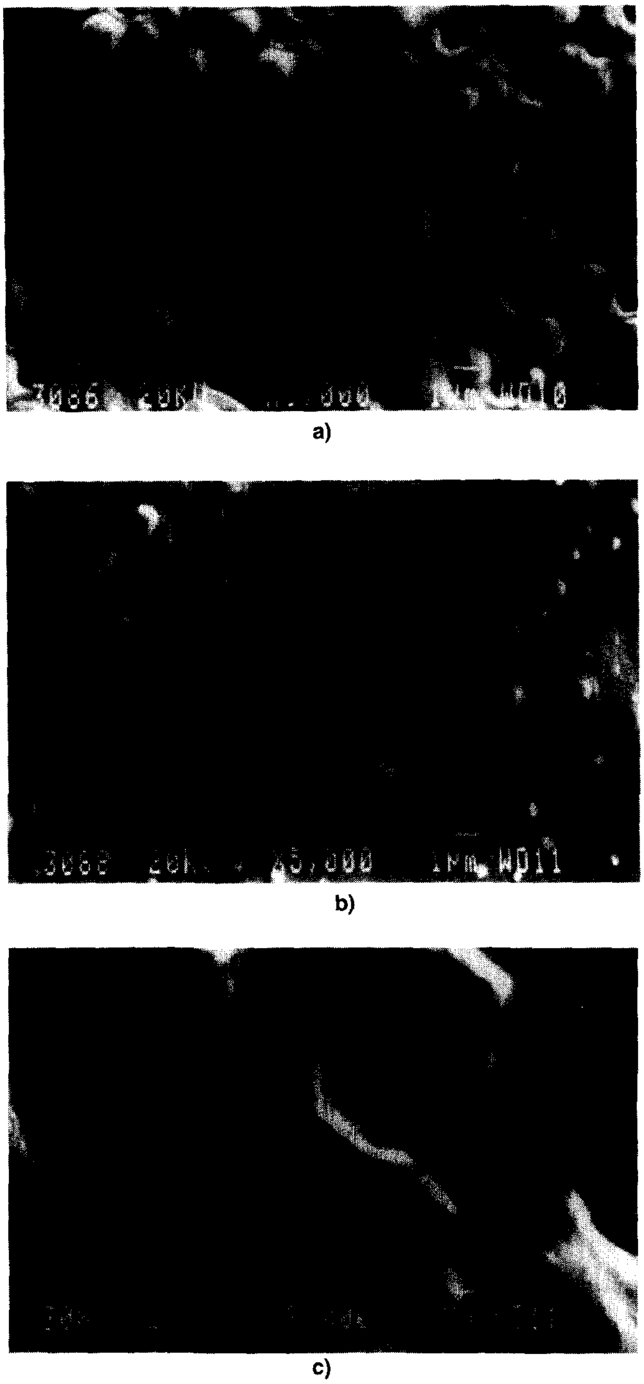


Figure 7 Appearance of samples obtained from ETINOX 450 and 45 phr of DOP heated to different temperatures: (a) 110°C: (b) 140°C; (c) 160°C

were in both cases very high, out of the range of the equipment, and the reproducibility was poor.

The shape of the curves obtained is strongly dependent on the type and concentration of the PVC resin, as expected. In all cases, it is possible to observe a similar trend: initially the plastisol has very low moduli; when the temperature increases, a progressive increase in both moduli is observed (obviously the velocity of increase in the moduli is directly related to the gelation velocity) up to a certain temperature where it starts to decrease, showing the end of the gelation process and the start of the thermal expansion and the fusion process. However, a closer study of the elastic modulus of the plastisols with the lower plasticizer concentration reveals, in the cases of ETINOX 440, ETINOX 450 and MIRVYL 1172, the presence of two successive increases



a)

b)

c)

Figure 8 Appearance of samples obtained from MIRVYL 1172 and 45 phr of DOP heated to different temperatures: (a) 110°C; (b) 140°C; (c) 160°C

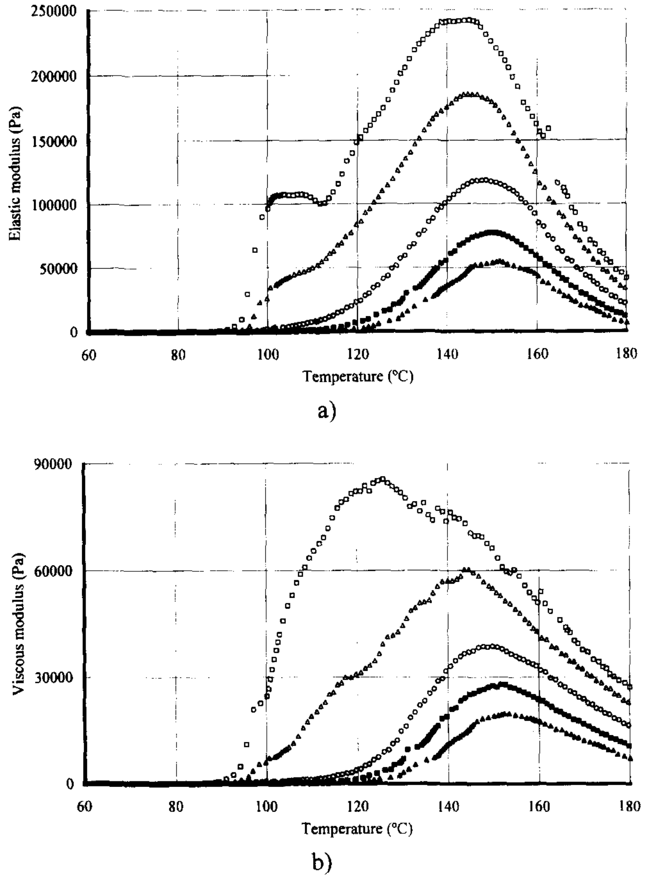


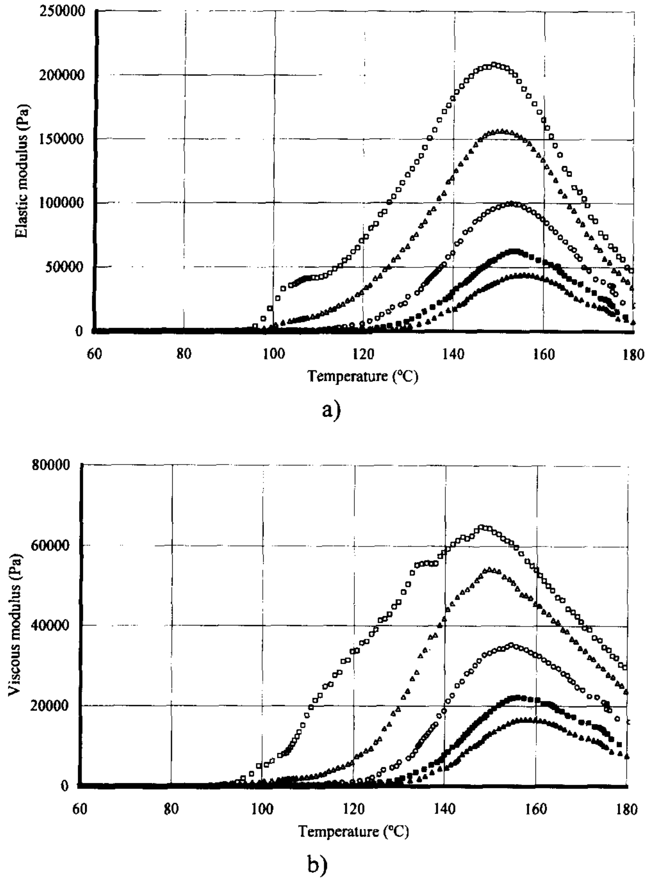
Figure 9 Behaviour of the elastic and viscous moduli for plastisols with ETINOX 450 and DINP: □ 45 phr; △ 50 phr; ○ 60 phr; ■ 70 phr; ▲ 80 phr

(with a different gelation velocity) which may correspond to two different steps in the gelation process, associated with the solvation of zones of the resin with a different dissolution velocity in the plasticizer, as already reported[2]. The first appears as a shoulder in the cases of the resins ETINOX 440 and ETINOX 450, or as a maximum with the resin MIRVYL 1172. Two different steps in the gelation process would be expected in plastisols with resins having a bimodal particle size distribution (like ETINOX 440, ETINOX 450 or HISPAVIC 367), and only one step in plastisols with a wide particle size distribution (like MIRVYL 1172); however, the behaviour observed does not correspond exactly with the behaviour expected since there are other important factors which can cause important deviations. The most important factors to be considered are differences in the type of resin (emulsion and microsuspension), differences in the internal structure of the particle, the presence of polymerization additives, etc., which explain the peculiar behaviour of the plastisols with MIRVYL 1172 with respect to the rest of the plastisols studied. Moreover, the plastisols with high concentrations of the resin HISPAVIC 367 seem to show only one step in the gelation process, but at higher concentrations of plasticizer (70 phr) it is possible clearly to observe two different steps; this behaviour can be due to the fact that in the plastisols with the higher resin concentration the first step is so marked that it overlaps the second, being almost invisible. Nevertheless, when the plasticizer concentration is increased and the first process is less marked, the second can be clearly observed.

Comparing the behaviour of the plastisols from the different resins studied, it is possible to order them according to the gelation velocity and to the moduli reached during gelation:

$$\text{ETINOX 440} < \text{ETINOX 450} < \text{HISPAVIC 367} < \text{MIRVYL 1172}$$

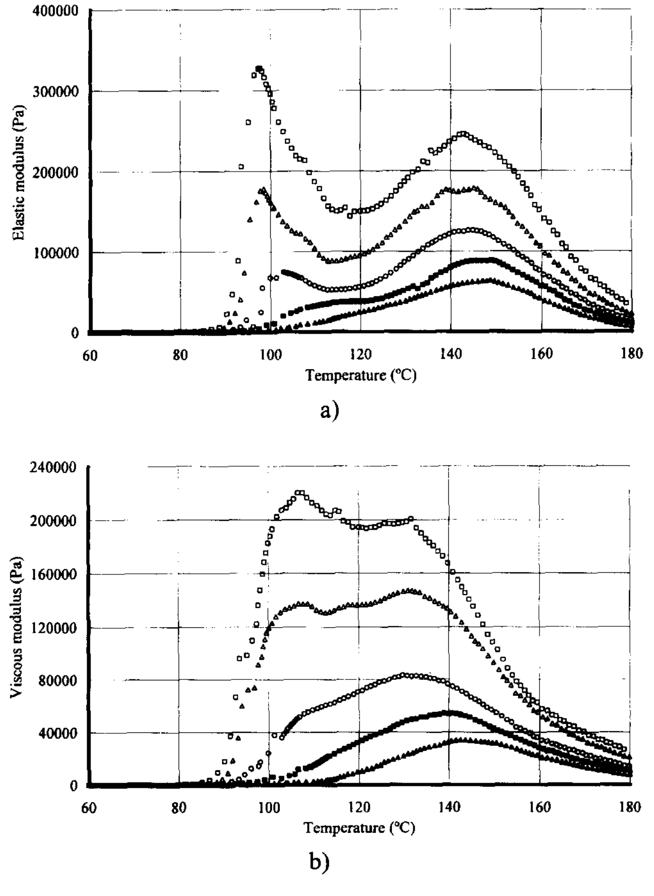
The order observed is the consequence of the superposition of two factors: the particle size and the molecular weight of the resin. In previous studies[2] it has been observed that an increase in particle size and molecular weight causes a decrease in the velocity of the gelation process as well as lower moduli reached during that process. However, some deviations from the expected behaviour can be observed if resins with a different concentration of polymerization



a)

b)

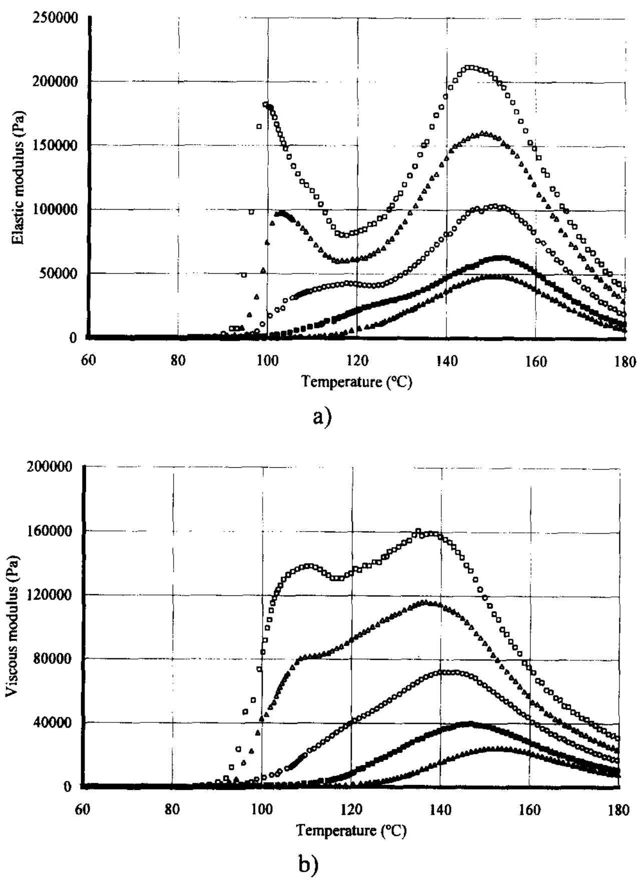
Figure 10 Behaviour of the elastic and viscous moduli for plastisols with ETINOX 450 and DIDP: □ 45 phr; △ 50 phr; ○ 60 phr; ■ 70 phr; ▲ 80 phr



a)

b)

Figure 11 Behaviour of the elastic and viscous moduli for plastisols with MIRVYL 1172 and DINP: □45 phr; △ 50 phr; ○ 60 phr; ■ 70 phr; ▲ 80 phr



a)

b)

Figure 12 Behaviour of the elastic and viscous moduli for plastisols with MIRVYL 1172 and DIDP: □ 45 phr; △ 50 phr; ○ 60 phr; ■ 70 phr; ▲ 80 phr

additives (e.g. emulsifier) or different inner morphology are used (this could be the case of emulsion resins with respect to microsuspension resins). In this way a plastisol with MIRVYL 1172 gels at lower temperatures, although its molecular weight is somewhat higher than that of the resins ETINOX 450 and HISPAVIC 367 and its particle size distribution includes bigger particles than the resin HISPAVIC 367. However, when comparing resins obtained by the same polymerization process with a very similar molecular weight (ETINOX 450 and HISPAVIC 367), it can be observed that the velocity of the gelation process and the moduli reached are higher in the resin with a higher number of small particles.

A closer observation of the viscous modulus behaviour (*Figures 3–6*) reveals the presence of three steps during the gelation process of the plastisols with higher concentrations of the resins MIRVYL 1172 (50–60 phr) and ETINOX 450 (45–60 phr). An additional step appears at temperatures between those corresponding to the two processes observed in the elastic modulus, which is more marked with decreasing plasticizer concentration. In the plastisol with 45 phr and 50 phr of DOP and both resins, it is so marked that it appears as a maximum. Moreover, this additional process in the viscous modulus is less marked if plasticizers with a lower solvent power (DINP or DIDP) are used with these resins (*Figures 9–12*). In this way, in the cases of the resin MIRVYL 1172 with 45–60 phr of DINP (*Figure 11*) and DIDP (*Figure 12*) and the resin ETINOX 450 with 45–50 phr of DINP (*Figure 9*) it is still observable, whereas with this resin and DIDP (*Figure 10*) it is less marked.

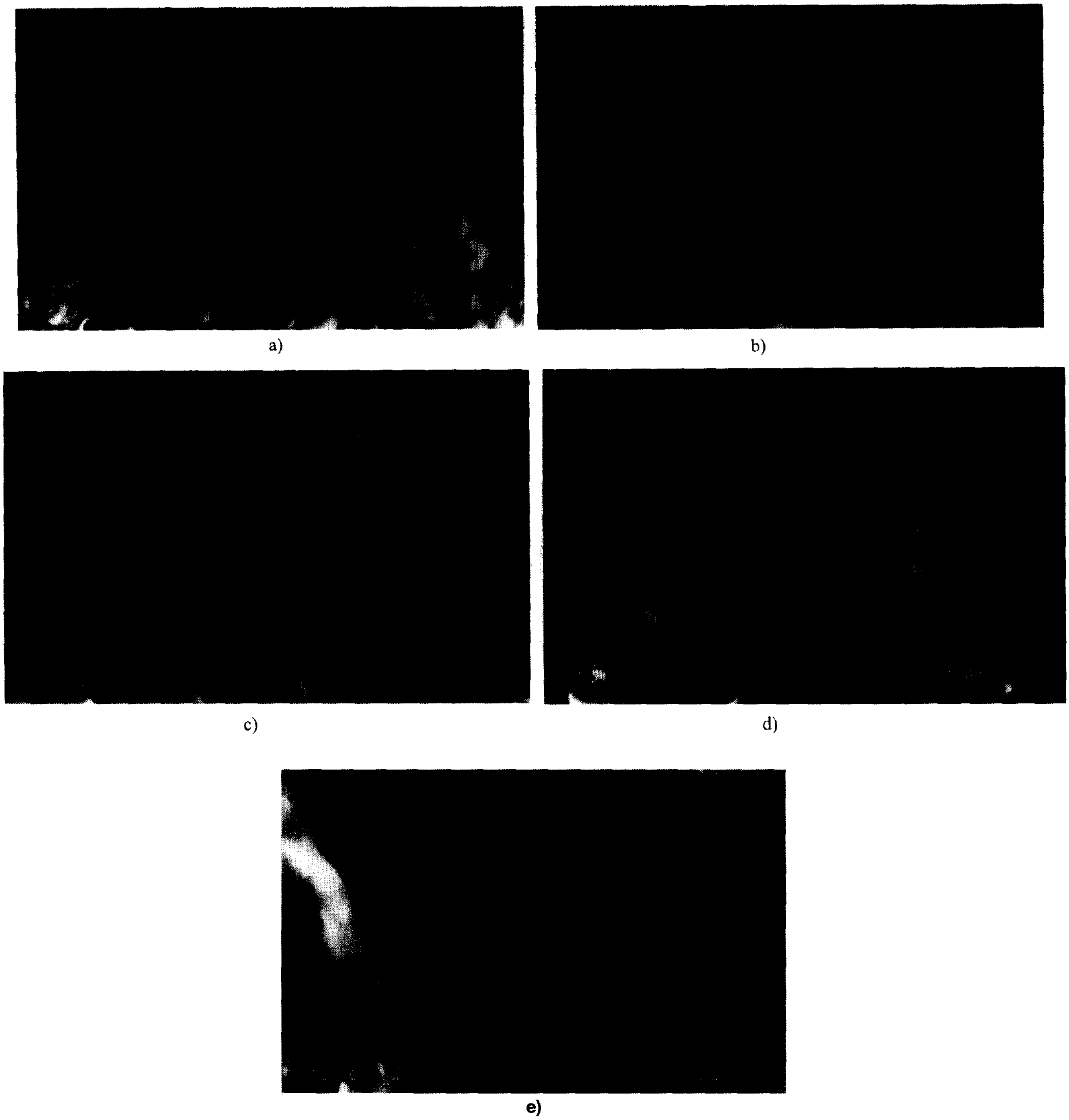


Figure 13 Aspect of samples obtained from MIRVYL 1172 and 45 phr of DIDP heated to different temperatures: (a) 90°C; (b) 100°C; (c) 110°C; (d) 140°C; (e) 160°C

The presence of the intermediate process of the viscous modulus, obviously associated with the presence of the PVC resin, has already been studied[13] and has been attributed to the contribution of the glass transition of the PVC resin, which mainly affects the viscous modulus of the plastisol. In order to explain this behaviour a qualitative model has been proposed, which considers that moduli of the plastisols are the result of the contribution of moduli of the discontinuous phase (i.e. the ungelled PVC particles) to moduli of the continuous phase (i.e. the gel obtained). This contribution depends on the cohesion between both phases. In this way, the contribution of the discontinuous phase to the global modulus of the plastisol is negligible if its proportion in the plastisol is low or when the cohesion between both phases is poor when the resin transition takes place. For example, in plastisols with resins which gel at high temperatures, such as ETINOX 440, the cohesion between both phases is too poor when the transition occurs to reflect it; on the other hand, in plastisols with resins which gel fast, such as the resin HISPAVIC 367, this process cannot be observed since the amount of ungelled resin when the transition occurs is too low to be observable in the moduli. Nevertheless, when gelation occurs at an adequate velocity so as to allow the observation of the transition, it is better observed in plastisols with plasticizers with higher compatibility with the PVC resin (i.e. DOP > DINP > DIDP), since they cause a stronger cohesion between the two phases.

On the other hand, from *Figures 9–12* it can be seen, as expected, that the use of lower solvation power plasticizers (DINP, DIDP) causes a delay in the gelation and fusion processes, and that the moduli reached during gelation are lower.

For further study of the gelation process, samples obtained from the resin MIRVYL 1172 with 45 phr of DIDP were heated to temperatures around the two maxima of the elastic modulus curve (90°C, 100°C, 110°C, 140°C and 160°C) and observed with a scanning electron microscope (*Figure 13*). Before the first maximum of the curve is reached (*Figure 13a*) it is possible to observe a relatively high number of particles which are joined by a small amount of continuous phase; if this image is compared with that of the PVC resin (*Figure 1*) it is noticeable that the smallest particles cannot be found in the heated plastisol, since they have been dissolved by the plasticizer. At temperatures very close to the first maximum (*Figure 13b*) there is a lower number of particles and the fraction of the continuous phase has increased. After the first maximum (*Figure 13c*) fewer particles are present in the plastisol and mainly particles of relatively large diameter (i.e. larger than $\sim 0.5\ \mu m$) can be observed. When the second maximum has been reached (*Figure 13d*) only a few particles of ungelled resin are present as a consequence of a further advance in the gelation process. However, after the second maximum (*Figure 13e*) it is practically possible to observe a uniform surface only where no particles of PVC resin are present, indicating that the gelation process has already finished. In conclusion, as can be stated from the microscope images, during the first step of the gelation process, the particles which dissolve faster in the plasticizer (mainly the smallest particles) have been incorporated into the continuous phase and, during the second step, the rest of the particles are then dissolved, yielding a homogeneous mass.

On the other hand, if images obtained from plastisols containing DOP (*Figure 8*) are compared with those corresponding to DIDP (*Figure 13*) it is noticed that, in the case of the plasticizer with a higher solvent power (DOP), the amount of continuous phase present at any temperature is higher, because gelation has reached a more advanced state.

CONCLUSIONS

The increase observed in elastic and viscous moduli correspond to the dissolution of the PVC particles whose size and number decrease progressively with temperature. Gelation can occur in several steps, depending on the velocity of dissolution of the PVC particles, and can cause successive increases in elastic and viscous moduli.

The use of progressively higher concentrations of plasticizer results in an increase in the temperature at which the gelation process concludes, producing less noticeable changes in the moduli curves.

An increase in the solvent power of the plasticizer, a decrease in its concentration as well as a decrease in the size of the PVC particles or in the molecular weight of the resin causes more noticeable changes in the behaviour of both moduli. A shift in the moduli curves *versus* temperature to higher temperatures has been observed on increasing the plasticizer concentration, the particle size or the molecular weight of the resin and decreasing the solvating power of the plasticizer. Moreover, an intermediate step between those observed in the elastic modulus appear in some of the viscous moduli curves, which shows the different ways in which both moduli reflect the processes occurring. The cause of this additional process is not well known and will be the object of further studies.

Scanning electronic microscopy (SEM) is a powerful complementary method capable of adding valuable information to that provided by other methods, such as rheology, thus providing a better understanding of the processes.

ACKNOWLEDGEMENTS

The authors wish to thank the Consellería de Educació i Ciència de la Generalitat Valenciana and FAMOSA (Fâbricas Asociadas de Muñecas de Onil S. A.).

REFERENCES

1. Nakajima, N. and Ward, D., *Rubb. Chem. Technol.*, 1981, **54**, 1096.
2. García, J. C. and Marcilla, A., Influence of the type of resin in the gelation and fusion processes of PVC plastisols. *Polymer* (accepted for publication).
3. Marcilla, A. and García, J. C., *Eur. Polym. J.*, 1997, **33**, 349.
4. Nakajima, N., Ward, D. W. and Collins, E. A., *Polym. Eng. Sci.*, 1979, **19**, 210.
5. Nakajima, N. and Daniels, C. A., *J. Appl. Polym. Sci.*, 1980, **25**, 2019.
6. Nakajima, N. and Ward, D. W., *J. Appl. Polym. Sci.*, 1983, **28**, 807.
7. Nakajima, N., Isner, J. D., Harrell, E. R. and Daniels, C. A., *Polym. J.*, 1981, **13**, 955.
8. Nakajima, N. and Harrell, E. R., *Adv. Polym. Technol.*, 1986, **6**, 409.
9. Nakajima, N. and Sadeghi, M. R., *Intern. Poly. Process. IV*, 1989, **1**, 16.
10. Nakajima, N. and Kwak, S.-Y., *J. Vinyl Technol.*, 1991, **13**, 212.
11. Marcilla, A. and García, J. C., *Eur. Polym. J.*, 1997, **33**, 357.
12. Nakajima, N., Isner, J. D. and Harrell, E. R., *J. Macromol. Sci.—Phys.*, 1981, **B20**(2), 349.
13. Marcilla, A. and García, J. C., Qualitative model for viscoelastic measurement during gelation and fusion of PVC plastisols. *Eur. Polym. J.* (accepted).