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The effect of adding processed PVC on the rheology of PVC plastisols

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In this paper the possibility of recycling the PVC resulting from the rotational moulding of plastisols is studied. Parts of processed PVC were ground with liquid nitrogen into four fractions of different sizes which were added to a plastisol at different concentrations. A study of the influence of the amount and size of the recycled PVC in the viscosity of the plastisol and in the gelation and fusion processes was carried out. Furthermore, samples were taken at different temperatures and observed by SEM (scanning electron microscopy). Results obtained for plastisols with the recycled PVC show a marked increase in the viscosity and moduli reached during gelation with time, which are more marked as the amount of recycled PVC increase and the particle size decrease. However, plastisols including recycled PVC show and adequate processability if they are used immediately after their preparation. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Few references have been found in the bibliography consulted concerning the recycling of PVC (particularly the case of plastisols). Only a few references have been found where PVC resulting from the processing of plastisols is employed, after grinding, in other processes (such as extrusion[1]). However, another possibility such as the recycling of the plasticized PVC in plastisols, after cryogenic grinding and sieving, would be an interesting proposal.

Rheology has proven to be a very suitable technique to study and characterize the behaviour of virgin plastisols in the gelation and fusion processes[2–10]. On the other hand, SEM is also a very valuable technique to observe the different state of these processes[11–14]. Thus, the objective of the present paper is to study the possibility of recycling processed PVC plastisols in PVC plastisols itself and analyse the influence of the particle size and its concentration in the gelation and fusion processes from the rheological and morphological point of view.

EXPERIMENTAL

Plastisols were prepared using the PVC resin ETINOX 450 from Aiscondel, the plasticizer Jayflex DOP (di-2-ethylhexyl phtalate) from Exxon and the thermal stabilizer ASUA 656 T2, from Industrias Quimicas ASUA (Spain). In all cases, the plastisols employed and recycled PVC had the same composition (i.e. 100 phr of the resin, 64 phr of the plasticizer and 6.4 phr of the stabilizer).

Recycled PVC was obtained from plastisols of the above composition heated at 200°C for 10 min. After grinding with liquid nitrogen four fractions of different average size (i.e. fraction 1, with a size smaller than 0.210 mm, fraction 2 with a size from 0.210 to 0.297 mm, fraction 3 with a size from 0.297 to 0.420 mm and fraction 4 with a size from 0.420 to 0.500 mm) were separated by sieving. Each fraction was added to the plastisols in three proportions: 1%, 5% and 10% in weight. Thus, all the plastisols including the recycled PVC particles have the same overall composition, but different amounts of recycled PVC particles of different particle size.

The viscosity of all the plastisols were determined in a BOHLIN CS 50 rheometer by means of viscometry tests using the 40 mm parallel plates, except in the case of plastisols with 10% of PVC, where the 20 mm parallel plates were used. However, in aged plastisols 20 mm parallel plates were always required.

In order to study the gelation and fusion processes, samples were loaded in the 20 mm parallel plates of the rheometer and oscillatory tests were carried out between 40 and 180°C with a heating rate of 10°C min^{-1}. A deformation amplitude of 0.005 and a oscillation frequency of 1 Hz were used.

Samples were taken at different temperatures (i.e. 110°C, 140°C and 160°C) and observed in a JEOL 840 JSM scanning electron microscope.

RESULTS

Study of the viscosity of the plastisols

Results obtained for the plastisols prepared with the different concentrations of recycled PVC (RPVC) are shown in *Figure 1*. A clear modification of the behaviour of the plastisol, even at the lowest percentage (1%) of adding can be observed. In all cases the viscosity of the plastisol increases, when increasing the RPVC concentration and when decreasing the particle size of the RPVC, following the expected behaviour when reducing the solids particle size and increasing concentration for any suspension[15]. On the other hand, it was observed that plastisols present a

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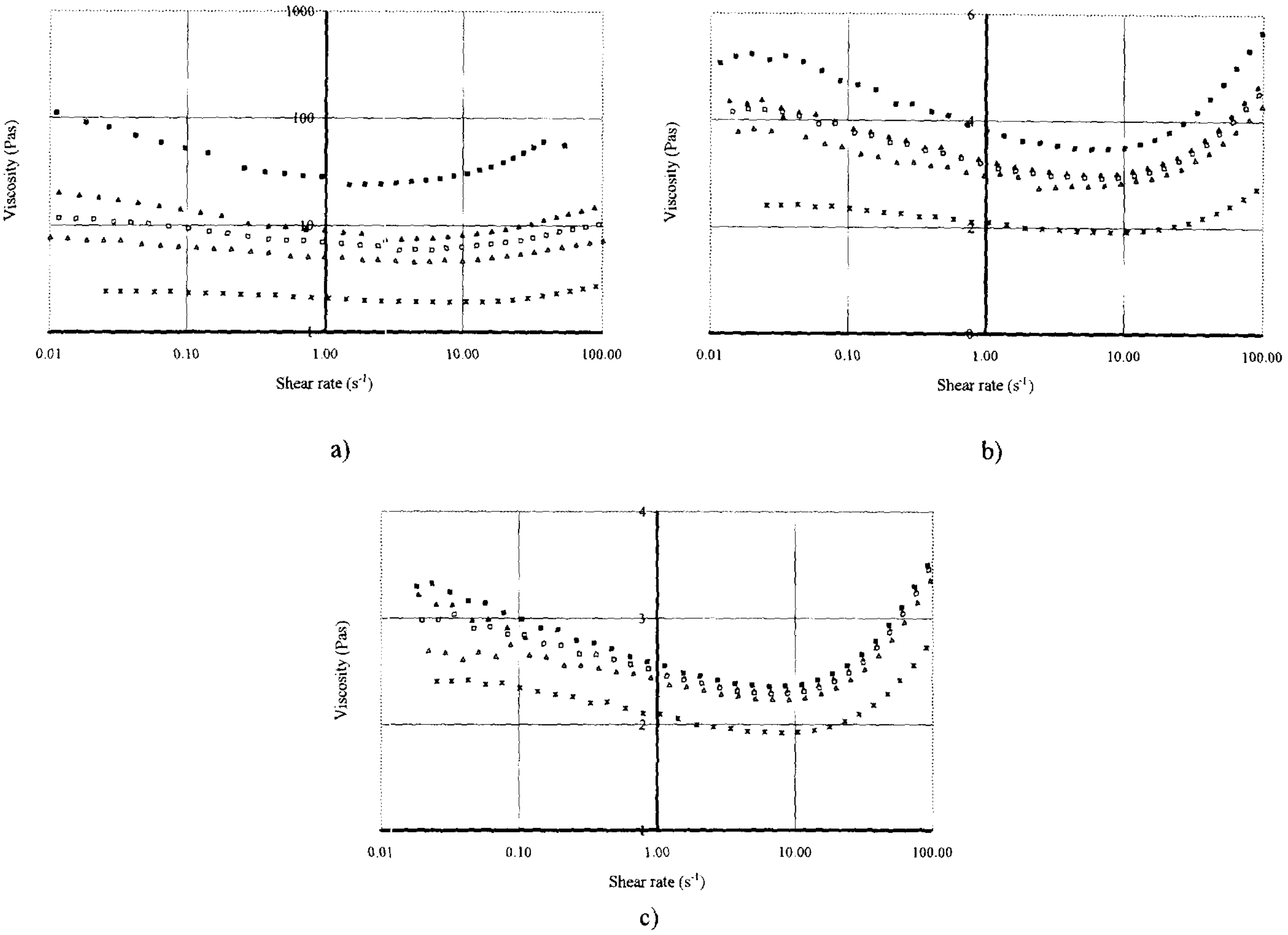


Figure 1 Behaviour of viscosity of plastisols with (a) 10%, (b) 5% and (c) 1% of recycled PVC: (■) fraction 1; (▲) fraction 2; (□) fraction 3; (△) fraction 4; (×) without recycled PVC

pseudoplastic behaviour at low and intermediate shear rates and dilatant behaviour at higher shear rates. Pseudoplastic behaviour can be due to the breakage of structures present in the suspension at rest, and consequently the resistance to flow is broken and the particles arrange themselves in more favourable patterns; however dilatancy can appear when particles of the suspension are pilled up, creating a resistance to flow. Both behaviours have been already observed and studied in PVC suspensions[15].

However, when plastisols are stored their viscosity increases quickly, probably due to the swelling and softening undergone by the RPVC particles. In this way, the viscosity of the plastisol was measured 24 h after its preparation (in all cases, the 20 mm parallel plates were required). The results obtained are shown in *Figure 2*. A marked increase in the viscosity of the plastisol can be observed in all cases. *Table 1* shows the viscosities at a shear rate of $1\ s^{-1}$ in order to compare the effect of the ageing time in the viscosity of plastisols. It can be observed that the changes in the viscosity with respect to the fresh plastisol are progressively more important as higher proportions of the smallest particles are employed.

These strong interactions must be taken into account when considering the possibility of processing those plastisols, including some RPVC. Plastisols including 10% of particle of size smaller than 0.210 mm have been successfully reprocessed in commercial products in similar processing conditions and with very similar end properties to those obtained from virgin plastisols.

Study of the gelation and fusion processes

Rheological study. Results obtained for the elastic and viscous moduli of plastisols with 10%, 5% and 1% of RPVC of the four fractions using the different fraction are shown in *Figures 3–5*, respectively.

It can be observed that at lower temperatures there is a marked increase in both elastic and viscous moduli when recycled PVC is added. This increase is pronounced as the amount of RPVC increases and the particle size decreases. For example, to reach an elastic modulus of 1000 Pa in the case of 10% of the smallest fraction (fraction 1) and in the higher proportion (10%), there is a difference of −17°C with respect to the virgin plastisol. This difference is −12°C for fraction 2, −11°C for fraction 3 and −10°C for fraction 4.

On the other hand, it can be also observed that the moduli reached are always higher when the smallest particles are added at the higher concentrations. The effect produced in the elastic modulus is noticeable even with 1% of RPVC added (*Figure 5*), producing a shoulder at approximately 100°C, which is more evident when increasing the concentration and when decreasing the particle size. This shoulder becomes a maximum for the extreme case of 10% of fraction 1 (*Figure 3*). With respect to the viscous modulus

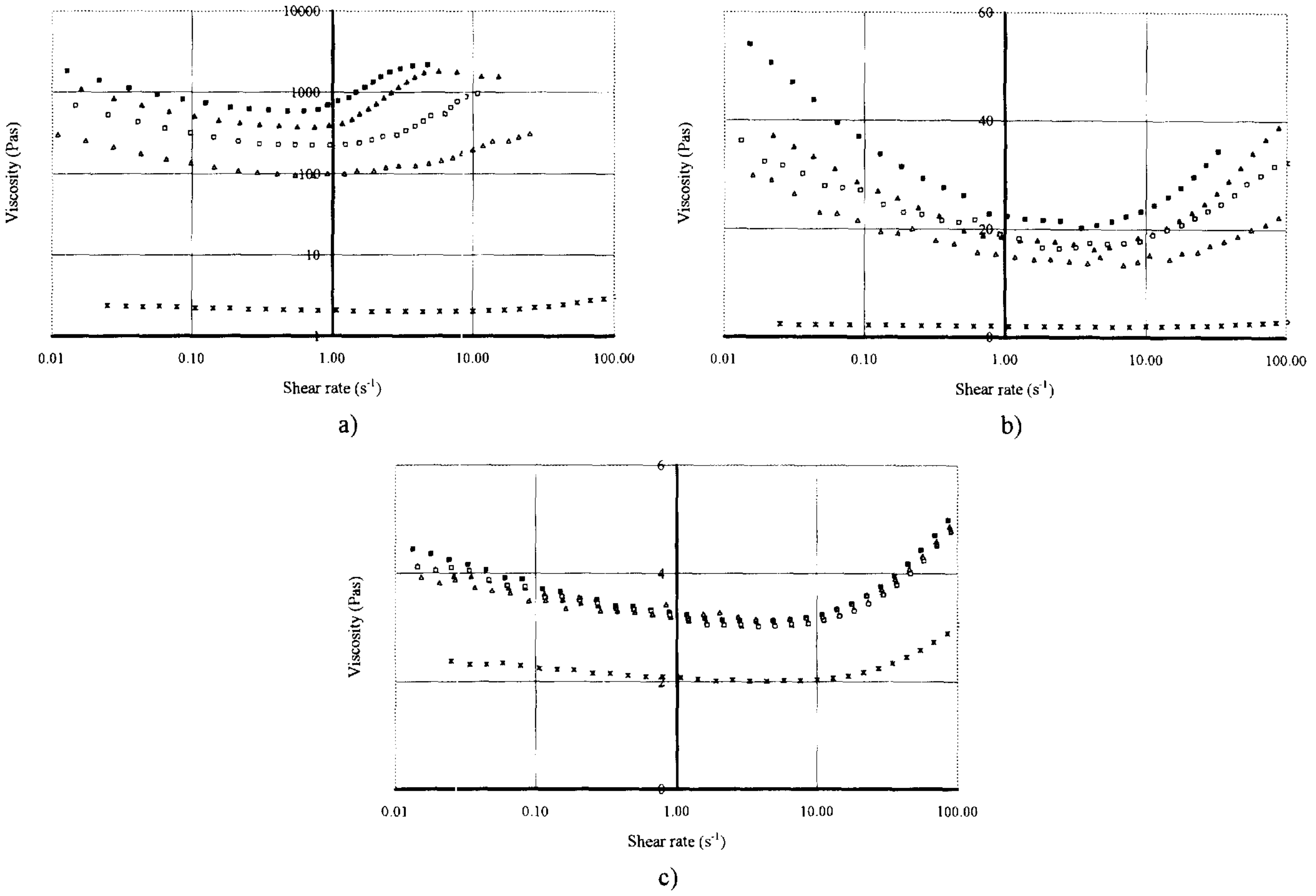


Figure 2 Behaviour of viscosity of aged plastisols with (a) 10%, (b) 5% and (c) 1% of recycled PVC: (■) fraction 1; (▲) fraction 2; (□) fraction 3; (△) fraction 4; (×) without recycled PVC

Table 1 Behaviour of viscosities (in Pas) at a shear rate of 1 s^{-1} for fresh and aged plastisols

Viscosity (Pas)	10%		5%		1%	
	0 h	24 h	0 h	24 h	0 h	24 h
Fraction 1	28.3	781	3.8	22.4	2.6	3.2
Fraction 2	9.0	395	3.2	20.2	2.5	3.2
Fraction 3	7.0	224	3.2	19.1	2.5	3.2
Fraction 4	5.1	101	3.0	14.9	2.4	3.2
Without any fraction	2.1	2.8	2.1	2.8	2.1	2.8

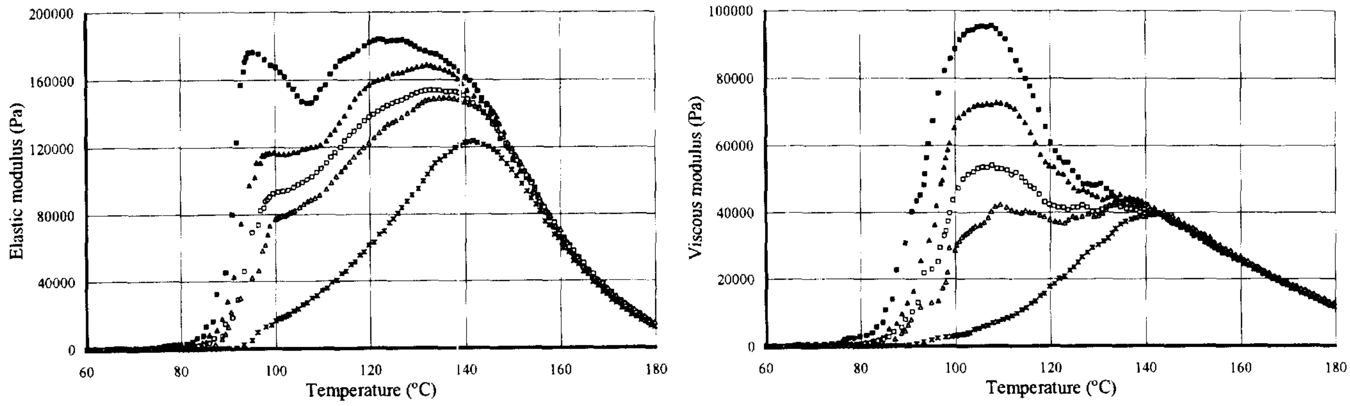


Figure 3 Behaviour of elastic and viscous moduli for plastisols with 10% of recycled PVC: (■) fraction 1; (▲) fraction 2; (□) fraction 3; (△) fraction 4; (×) without recycled PVC

the addition of RPVC produces the same effect, but at 5% of fraction 1 (*Figure 4*) the shoulder is already a maximum.

The maximum (or the shoulder) in the elastic modulus is the result of the interaction between the continuous phase of the gelling plastisol (i.e. the plasticizer and the progressively dissolved resin) and the RPVC particles. Such particles already include 64 phr of plasticizer, and consequently their interaction or dissolution with the

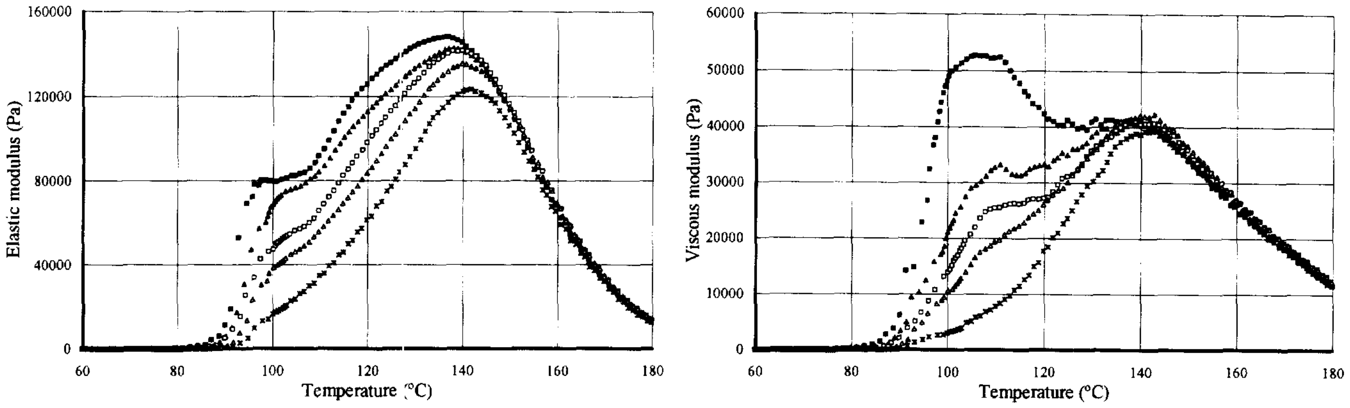


Figure 4 Behaviour of elastic and viscous moduli for plastisols with 5% of recycled PVC: (■) fraction 1; (▲) fraction 2; (□) fraction 3; (△) fraction 4; (×) without recycled PVC

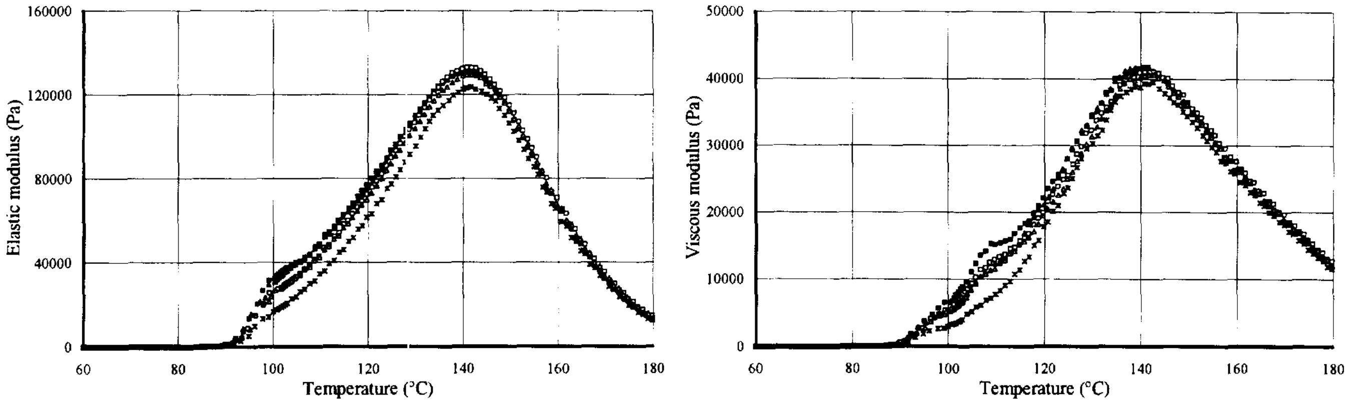


Figure 5 Behaviour of elastic and viscous moduli for plastisols with 1% of recycled PVC: (■) fraction 1; (▲) fraction 2; (□) fraction 3; (△) fraction 4; (×) without recycled PVC

plasticizer should be clearly favoured with respect to the virgin PVC and less plasticizer would remain available in the continuous phase to interact with the virgin PVC. Thus, the net effect could be as that observed for a plastisol with a lower amount of plasticizer. On the other hand, the moduli of the RPVC particles is higher than that of the continuous phase, and their contribution to the global moduli may also be responsible for the observed increase. After this process, if the concentration of the RPVC is high (10%), the elastic modulus marks a maximum since the decrease produced by the temperature effect predominates over the increase due to the gelation process. However, if the concentration is lower (1% or 5%) the effect of the gelation process is more important and the plastisols show trends more similar to the virgin plastisols.

The viscous modulus show the same trend as the elastic modulus. Nevertheless, the presence of the particles of RPVC is more obvious than in the elastic modulus, producing (as expected) a marked effect when decreasing the particle size or increasing the concentration (as expected).

However, when fusion progresses the moduli (both elastic and viscous) of all the plastisols show a behaviour progressively closer to that of the virgin plastisol, indicating that the initial structure of the suspension is disappearing. Once this structure has disappeared all samples present the same moduli, as expected for plastisols with the same composition.

As a comparison, the influence of the ageing time in the behaviour of plastisols during gelation and fusion was studied. For this purpose viscoelastic measurements were repeated on plastisols stored for 24 h at room temperature. Results obtained for aged plastisols are shown in *Figures 6–8*.

A very different behaviour can be observed when comparing these figures with those of the fresh plastisols (*Figures 3–5*). With respect to the more concentrate plastisols (10% or 5%, see *Figures 6 and 7*) it is possible to observe that both moduli have a maximum at approximately 100°C. This temperature coincides with that of the shoulder observed in the fresh plastisol (*Figures 3 and 4*). A similar behaviour can be observed for the viscous modulus in all fractions. Moreover, in plastisols with 5% and 1% (*Figures 7 and 8*) of RPVC the same processes can be observed as in plastisols with 10% (*Figure 6*), though less marked, according to their concentration. It can be concluded that both in fresh plastisols and in aged plastisols, softening and swelling suffered by the particles of ground PVC takes place; nevertheless, in the aged plastisols they are easier to produce and yield stronger interactions between the plastisol which is gelling and the RPVC particles.

On the other hand, in plastisols with 10% and 5% of RPVC (*Figures 6 and 7*) no relation between the modulus maximum of the curves and the particle size of RPVC was observed. This was probably due to the deformation suffered by the RPVC particles during the ageing time as a consequence of the swelling and softening processes which clearly occur in that period. Despite this, the elastic and viscous moduli of aged plastisols with the same concentration follow very similar behaviours: both moduli

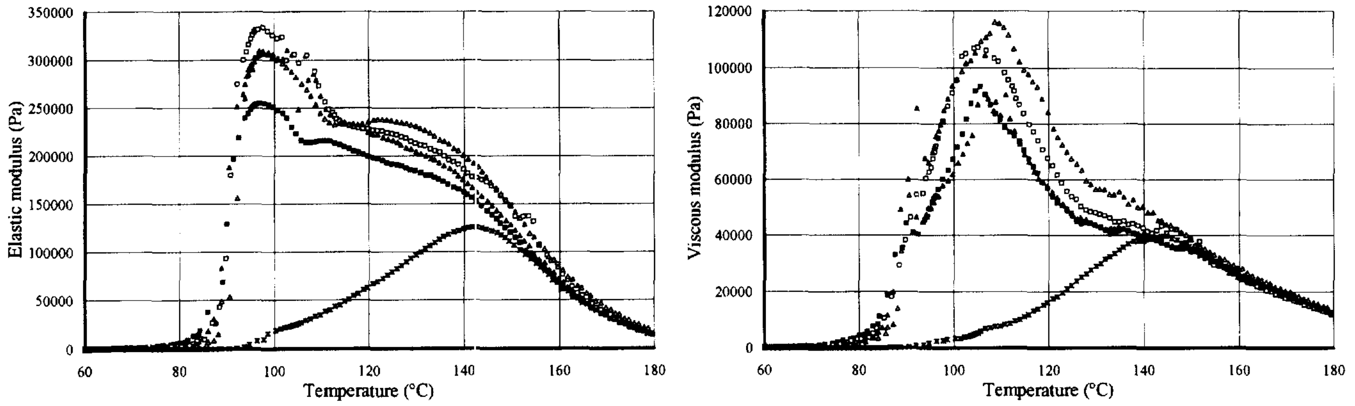


Figure 6 Behaviour of elastic and viscous moduli for aged plastisols with 10% of recycled PVC: (■) fraction 1; (▲) faction 2; (□) fraction 3; (△) fraction 4; (×) without recycled PVC

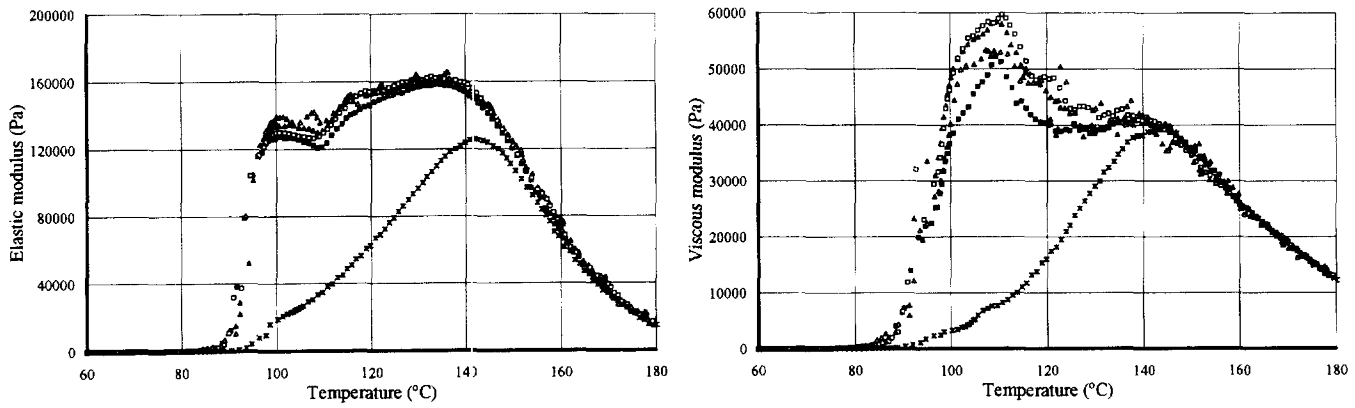


Figure 7 Behaviour of elastic and viscous moduli for aged plastisols with 5% of recycled PVC: (■) fraction 1; (▲) fraction 2; (□) fraction 3; (△) fraction 4; (×) without recycled PVC

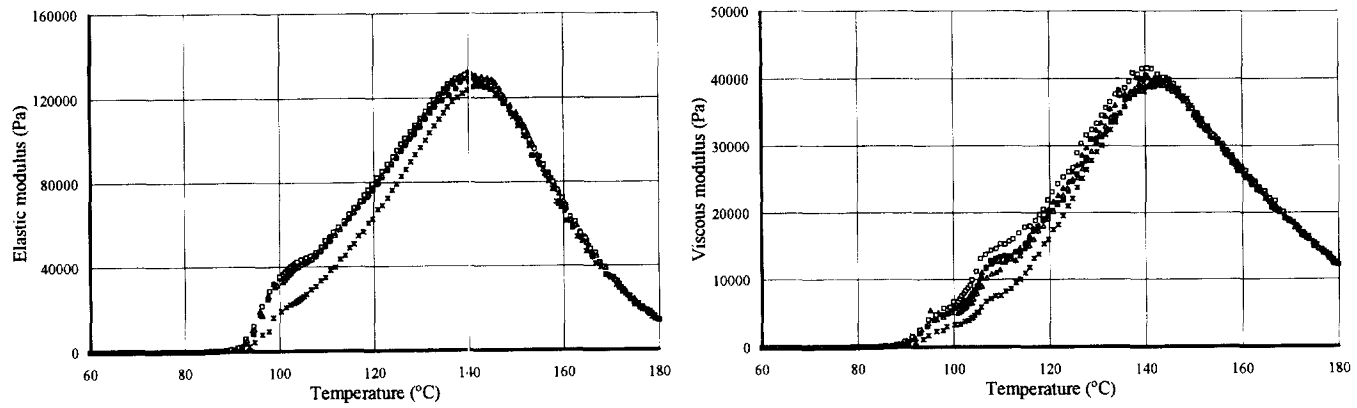


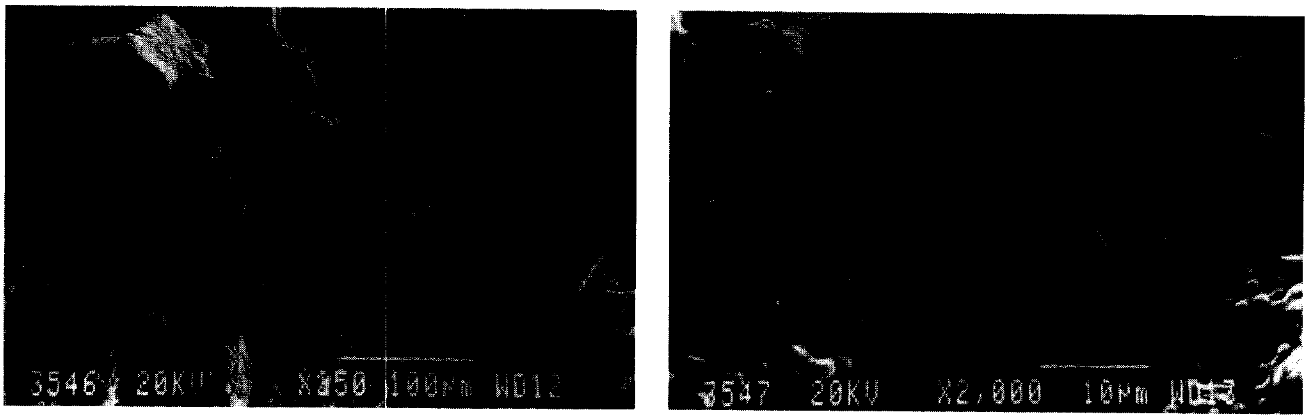
Figure 8 Behaviour of elastic and viscous moduli for plastisols with 1% of recycled PVC: (■) fraction 1; (▲) fraction 2; (□) fraction 3; (△) fraction 4; (×) without recycled PVC

reach a maximum, or a shoulder. Afterwards, they decrease or increase (depending on the RPVC concentration) to reach values closer to the virgin plastisol, indicating once again that at this point the initial structure of the suspension has disappeared.

Finally, it can also be observed in *Figures 6–8* that in aged plastisols gelation is notably advanced with respect to the fresh plastisols or with respect to the plastisols including only virgin PVC particles, since both moduli start to increase at lower temperatures, clearly showing that the swelling and gelation occur much sooner in the RPVC particles.

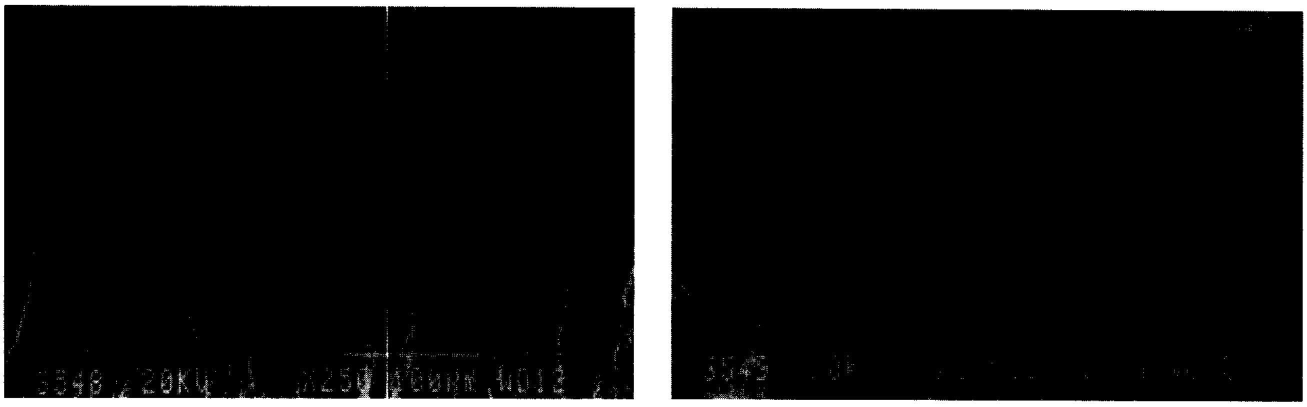
Morphological study. To study the morphological changes undergone by the particles of the RPVC during the second gelation process, some samples were obtained in the rheometer at different temperatures (110°C, 140°C and 160°C) and cooled. Afterwards these samples were broken up after immersion in liquid nitrogen and the fracture surfaces were observed in a microscope. Samples were obtained from the four different fractions mentioned above, but no differences were observed, regardless of the different particle size.

At 110°C [*Figure 9*(a) at ×250 magnification) it is possible to distinguish the presence of RPVC particles. A



a) b)

Figure 9 Aspect of plastisol with fraction 1 heated to 110°C at: (a) ×250 magnification; (b) ×2000 magnification



a) b)

Figure 10 Aspect of plastisol with fraction 1 heated to 140°C at: (a) ×250 magnification; (b) ×2000 magnification

closer inspection (at ×2000 magnification) reveals clear differences between fracture surface of the continuous phase of the gelling plastisol and that of the RPVC particles [*Figure 9*(b)]. Nevertheless, there is not a sharp parting line at the interface, showing the interaction between the plastisol and the RPVC particles.

At higher temperatures (at 140°C) the aspect at ×250 magnification [*Figure 10*(a)] and ×2000 magnification [*Figure 10*(b)] of the two surfaces (those corresponding to the plastisol which is gelling and the RPVC) is more uniform as a consequence of an advance in the gelation process and a further interaction between them.

Finally, at 160°C (*Figure 11*) it is not possible to distinguish any mark corresponding to the RPVC particles, indicating that at this point the particulated structure of the RPVC plastisol has disappeared and that there is a total compatibility between the fresh plastisol and the RPVC.

CONCLUSIONS

The flow properties of the plastisols are considerably modified by the presence of particles of recycled PVC, even when a low proportion is added (1%). Particle size strongly determines the plastisol viscosity and the smaller particles yield the higher viscosity. However, the viscosity of the plastisols obtained still allows the application of these plastisols in rotational moulding if used immediately after their preparation.

Ageing time strongly increases the viscosity of these plastisols as a result of the favoured interactions between the fresh plasticizer and the RPVC particles.

During the gelation of these plastisols, those with a higher amount of the smallest particles develop higher moduli than those with the lower proportion of particles or the same

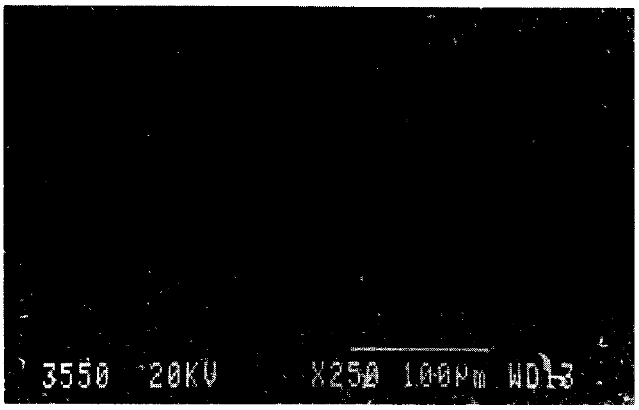


Figure 11 Aspect of plastisol with fraction 1 heated to 160°C at × 250 magnification

proportion of bigger particles. However, when fusion progresses the moduli of all plastisols are very similar, proving that the initial structure of the suspension has almost disappeared and all plastisols behave in a similar way as expected for plastisols of the same overall composition.

Ageing time also affects the properties of the plastisols during the gelation, accelerating considerably the process and yielding higher moduli than the fresh plastisols.

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