



## PVC PLASTISOLS DECOMPOSITION BY FT-IR SPECTROSCOPY

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**Abstract**—A specially designed cell, as described in previous papers, has been used to study the dynamic *in situ* decomposition of PVC plastisols by FT-IR. The FT-IR spectra provides a new point of view into the intricate problem of the effect of the plasticizers (compatibility and concentration) in the PVC decomposition. A qualitative description of the changes observed in the plastisols spectra is presented. Firstly, the bands due to the plasticizer disappear at temperatures in good accordance with those observed for the plasticizer evaporation in the thermogravimetric decomposition of the PVC plastisol. The plasticizer evaporation leads to a spectrum very similar to that obtained when the PVC is alone at the same temperature. After plasticizer evaporation changes observed in plastisols decomposition are similar to those previously reported with respect to resins decomposition. © 1997 Elsevier Science Ltd

### 1. INTRODUCTION

The effect of plasticizers on the decomposition of PVC is a complex phenomenon which is still not well understood and the results and conclusions obtained and stated by different authors may be markedly different. Most of the papers on topics related to this refer to the thermal stability of plasticized PVC, but not on the effect of the plasticizer on the thermal stability of PVC. From this point of view, the thermal stability of plasticized PVC decreases when increasing the volatility of the plasticizer used [1–2].

Marcilla and Beltrán found by TG [3–4] that the evolution of the plasticizers from plastisol samples took place at temperatures somewhat higher than from samples where the contact between the PVC and the plasticizer was avoided. The plasticizer is adsorbed by the resin in the plastisols during the gelation process, consequently delaying its evolution. On the other hand, the decomposition of the PVC from plastisol samples occurs at temperatures lower than those when the PVC and the DOP are separated in the sample holder. It was concluded that the presence of the DOP accelerates the process of decomposition of the PVC. These results are in good agreement with those obtained by other authors, in the sense that the addition of polar compounds to the PVC results in a destabilizing effect [5]. This effect increases when increasing the compatibility of the plasticizer. Moskala and Lee [6] observed that the evolution of the acids (i.e. acetic and chlorhydric acid) from mixtures of PVC/EVA and PVC/PVA occurs at lower temperatures from the mixtures than from the separated polymers. The effect is more marked when increasing the miscibility of the mixture. Millán *et al.* [7] showed that the mixture of PVC with an incompatible polymer does not affect its stability. Nevertheless, the mixture with a compatible

highly rigid polymer, such as the PCL poly( $\epsilon$ -caprolactone), hinders the movement of the GTTG<sup>−</sup> conformations in the PVC, resulting in a stabilizing effect.

Minsker *et al.* [8] observed that the rate of PVC degradation increases when using plasticizers of the alkyl and alkyl-aryl phosphate type. This effect is considered to be due to their high nucleophilic character. In latter works Minsker *et al.* [9] tested that the addition of even small amounts of phthalates, sebasates and adipates to PVC decreases the rate of dehydrochlorination, due to an inhibition effect on the growing of the polyene sequences. The ester groups of plasticizers solvate the labile groups of the polymer chain, which are responsible for the instability (i.e. the carbonyl allylic groups, according to Minsker), avoiding double-bond formation. The more compatible plasticizers (in a given family) are those producing a stronger dehydrochlorination effect. On the other hand, the presence of plasticizers based on carboxylic groups accelerates the thermo-oxidative degradation of the PVC. These plasticizers are oxidized to peroxides which accelerate the decomposition of the PVC [10].

On the contrary, Kovacic *et al.* [11] obtained results very different to those obtained by Minsker. They found that the rate of dehydrochlorination of PVC plasticized by DOP was almost unaltered, whereas when using 2-ethylhexyl phosphate as plasticizer, this rate was lower due to a stabilizing effect of this compound.

According to Wypych [1], the plasticizer normally used in the formulations of the plastisols can be included in either of the two following groups: dioctylphthalate, dioctylazelate, diisooctyl adipate, which increase the thermal stability of the polymer and butylbenzyl phthalate, diphenyl octyl phosphate and tricresyl phosphate, which decrease the thermal stability of the polymer.

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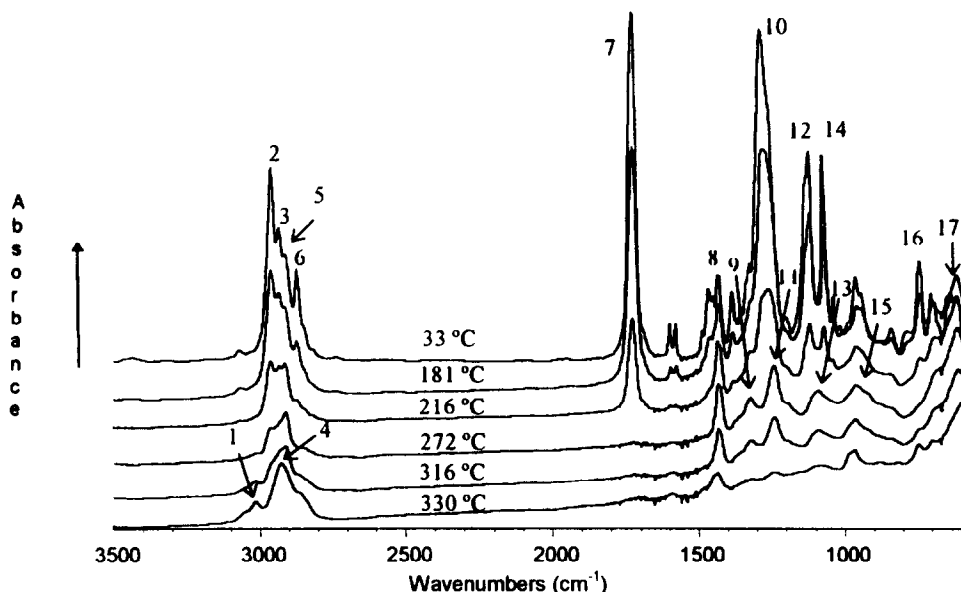


Fig. 1. Spectra of the plastisol with 65 phr of DBP at 33, 181, 216, 272, 316 and 330°.

The behaviour of the PVC plastisols during the processes of gelation and fusion was studied in previous works [12, 13], by the FT-IR technique and obtaining the IR spectra *in situ*, in a specially designed cell and sample holder. In these researches the effect of the plasticizer on the IR spectrum of the resin was observed, as a consequence of the interactions established among them. In another paper, we reported on the pyrolysis of two commercial PVC resins from the IR spectra obtained in the same device [14]. In this way, the great utility of this IR cell and sample holder was confirmed to obtain *in situ* the IR spectra of the sample under dynamic conditions. The objective of the present work is to study the pyrolysis of PVC plastisols from the point of view provided by the FT-IR technique previously developed, where the spectra of the different residues are obtained *in situ* in a specially designed device. In addition, the effect of different plasticizers of the phthalates family and the effect of the concentration is also considered.

## 2. EXPERIMENTAL

The emulsion PVC resin Etinox 450 (E450) from Aisconcel, was used in all the plastisols formulations. The average molecular weight of this resin was  $M_w = 101,000$ , and the polydispersity ratio  $M_w/M_n = 2.91$ . Diisobutyl phthalate (DBP), di-2-ethylhexyl phthalate (DOP) and diisodecyl phthalate (DIDP) were used as plasticizers. The boiling ranges at 5 mbar (according to the suppliers) were 180–186, 230–233 and 250–267°, respectively. The plastisols were prepared with 65 phr of each plasticizer and with 40, 65 and 90 phr, in the case of DOP. No stabilizers were used.

A Nicolet 510 FT-IR was used, which was controlled by a 680 spectral workstation from Nicolet. The evolution of PVC and plastisol spectra during heating was followed, employing the programmable temperature liquid transmission cell HT-32 from Nicolet. The system was controlled to take one interferogram each 15 sec and 10 scans by interferogram, the resolution was set at  $4\text{ cm}^{-1}$ , and gain 1. The heating rate was  $10^\circ/\text{min}$ , from room temperature up to  $340^\circ$ . Nitrogen of 99.999% purity at a flow rate of 100 mL/min was used as the purge. More details about the

Table I. Position of the bands ( $\text{cm}^{-1}$ ) of the spectra of the plasticizer (DBP), the resin E450 and the plastisol at 33, 181, 201, 211, 216, 221, 242, 272, 300°C

|    | DBP    | PVC    | 33     | 181    | 201    | 211    | 216    | 221    | 242    | 272    | 300    | 316    | 330    |
|----|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1  | —      | —      | —      | —      | —      | —      | —      | —      | —      | —      | 3014.8 | 3015.3 | 3014.4 |
| 2  | 2961.1 | 2971.4 | 2961.4 | 2961.7 | 2961.8 | 2961.9 | 2962.1 | 2963.3 | 2964.1 | 2963.5 | —      | —      | —      |
| 3  | 2935.7 | —      | 2935.2 | 2934.9 | 2934.8 | 2934.0 | 2932.2 | —      | —      | —      | —      | —      | —      |
| 4  | —      | —      | —      | —      | —      | —      | —      | —      | —      | —      | —      | —      | 2926.9 |
| 5  | —      | 2912.1 | 2914.1 | 2915.1 | 2915.1 | 2914.0 | 2913.2 | 2912.6 | 2912.4 | 2912.4 | 2912.6 | 2912.6 | —      |
| 6  | 2874.8 | —      | 2874.7 | 2874.9 | 2875   | 2874.9 | 2874.8 | —      | —      | —      | —      | —      | —      |
| 7  | 1728.3 | —      | 1731.4 | 1728.5 | 1728.4 | 1728.1 | 1727.7 | 1726.8 | —      | —      | —      | —      | —      |
| 8  | —      | 1434.8 | 1434.7 | 1434.7 | 1434.3 | 1433.9 | 1433.5 | 1433.2 | 1432.9 | 1432.8 | 1432.7 | 1432.4 | 1432.6 |
| 9  | —      | 1333.6 | —      | —      | —      | —      | 1321.8 | 1322.4 | 1322.3 | 1321.8 | 1321.6 | 1320.6 | —      |
| 10 | 1286.6 | —      | 1286.9 | 1279.5 | 1278.9 | 1271.1 | —      | —      | —      | —      | —      | —      | —      |
| 11 | —      | 1254.4 | —      | —      | —      | —      | 1257.4 | 1247.7 | 1242.9 | 1242.0 | 1241.6 | 1240.7 | 1238.0 |
| 12 | 1122.7 | —      | 1122.5 | 1120.7 | 1120.2 | 1120.0 | 1119.0 | 1116.0 | —      | —      | —      | —      | —      |
| 13 | —      | 1099.0 | —      | —      | —      | —      | —      | —      | 1092.7 | 1091.1 | 1090.8 | 1090.6 | —      |
| 14 | 1074.6 | —      | 1070.8 | 1070.4 | 1070.3 | 1070.3 | 1070.6 | —      | —      | —      | —      | —      | —      |
| 15 | —      | 960.8  | 962.8  | 958.7  | 958.4  | 958.3  | 959.0  | 959.0  | 959.3  | 962.0  | 962.9  | 964.1  | 964.9  |
| 16 | 744.9  | —      | 744.6  | 742.2  | 741.7  | 741.6  | —      | —      | —      | —      | —      | —      | 742.0  |
| 17 | —      | 616.5  | 614.5  | 613.8  | 613.6  | 613.6  | 614.5  | 613.0  | 614.1  | 611.7  | 610.7  | 609.9  | —      |

sample cell and experimental conditions can be found elsewhere [14].

The thermogravimetric analysis of the plastisols was carried out in a TGA 7 Perkin-Elmer apparatus at a heating rate of 10°/min. More details of the equipment and experimental conditions used can be found elsewhere [4].

### 3. RESULTS AND DISCUSSION

#### 3.1. Pyrolysis of PVC plastisols

Figure 1 shows a series of spectra corresponding to the plastisol with DBP at increasing temperatures between 33 and 330°. The location where the bands marked in Fig. 1 appear is shown in Table 1. This table also includes the location of the absorption bands corresponding to the resin and the plasticizer at room temperature. The spectrum of the plastisol at room temperature is almost coincident with that of the plasticizer. The contribution of the resin to the spectrum of the plastisols is very small and can only be observed in the bands at 1427 and 1435 cm<sup>-1</sup> corresponding to methylene groups and in the bands in the region at 600–700 cm<sup>-1</sup>, due to C—Cl groups of the resin, as was reported elsewhere.

In the sequence of spectra in Fig. 1 and Table 1, it can be observed that between 180 and 330°, a great number of significant modifications is produced, in both the position and shape of the absorption bands. Below 180° the modifications are lower and are related to the gelation and fusion processes as previously discussed [13]. The modifications produced at temperatures above 180° are higher and are related to the pyrolysis of the plastisol.

**3.1.1. Pyrolysis of the plastisol E450-DBP below 270°.** Table 1 shows how, between 216 and 242°, the bands 3, 6, 7, 10, 12, 14 and 16, whose origin is the plasticizer, disappear. The position of these bands is modified very slightly before their disappearance, except for bands 10, 12 and 14, which overlap with other bands which appear, at close wavenumbers, and are due to the resin. In Fig. 1 other absorption bands can also be observed, such as the doublet corresponding to the aromatic ring of the plasticizer (around 1580 cm<sup>-1</sup>) and other small bands corresponding to the plasticizer, which disappear together with those already mentioned.

Figure 2 shows a magnification of the spectra between 33 and 242°, where the loss of the plasticizer can be clearly observed in all the regions of the spectrum. Between 33 and 181°, only a small decrease of the intensity of the DBP is apparent. Nevertheless, between 181 and 221°, great modifications of the spectra occur, as a consequence of the intensive loss of the plasticizer. The evaporation and consequent loss of the plasticizer is especially apparent in the band corresponding to the carbonyl group at 1728 cm<sup>-1</sup> [Fig. 2(b)], since this band, corresponding to the plasticizer, does not overlap with any band of the resin. The spectrum at 242° shows the complete disappearance of this and all bands corresponding to the plasticizer.

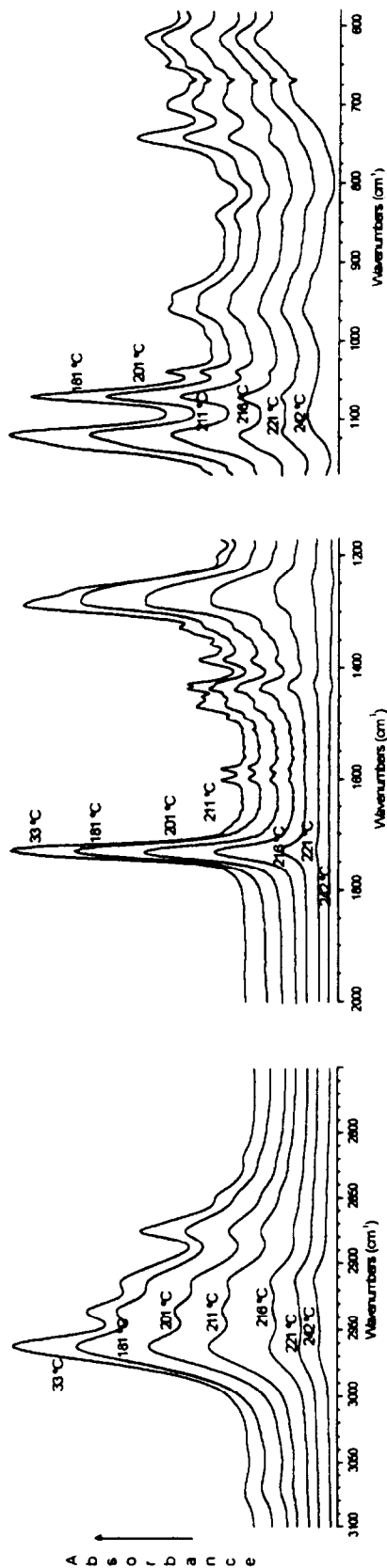


Fig. 2. Spectra of the plastisol with 65 phr of DBP at 33, 181, 201, 211, 216, 221 and 242° (a) between 3200 and 2700 cm<sup>-1</sup>, (b) between 2000 and 1150 cm<sup>-1</sup>, and (c) between 1170 and 580 cm<sup>-1</sup>.

The spectrum of the resin was masked by that of the plasticizer and gradually appeared as the evaporation of the plasticizer proceeded. During the pyrolysis of the resins up to  $270^{\circ}$ , a displacement of the bands involving chlorine atoms was observed elsewhere [14]. In the plastisol, such displacements cannot be observed due to the presence of the plasticizer. Nevertheless, the spectrum at  $242^{\circ}$ , where the bands from the plasticizer have completely disappeared, is very similar to that of the resin at this temperature. This fact can be clearly observed in Fig. 3, where the spectra corresponding to the resin E450 and the plastisol with DBP, at  $240^{\circ}$ , are compared. The shape and position of most of the bands in both spectra is very similar, although some differences exist in the relative intensity of certain bands. Considering the methylene band at  $1435\text{ cm}^{-1}$  as a reference, a decrease is observed in the relative intensity of the bands at  $2964$  and  $1325\text{ cm}^{-1}$ , corresponding to C—H stretching of the group  $\text{ClC—H}$  in the plastisol spectrum. On the other hand, a clear increase in the intensity of the bands at  $1243$  and  $614\text{ cm}^{-1}$ , corresponding to  $\text{ClC—H}$  and C—Cl stretching, can also be observed. These facts reveal the interactions between the plasticizer and the resin during this process. Between  $240$  and  $270^{\circ}$ , the spectra of plastisol suffer almost no modifications (Table I), in a way similar to that observed during the pyrolysis of the resins. For this reason, the spectrum corresponding to this temperature has not been included in the figures, because it is almost identical to that at  $240^{\circ}$ .

**3.1.2. The pyrolysis of the plastisol E450-DBP above  $270^{\circ}$ .** After the evolution of the plasticizer, the residue obtained is very similar to that obtained from the resins at the same temperature. Figure 4 shows the evolution of the spectra of the plastisol at temperatures above  $270^{\circ}$  in the region between  $3200$  and  $2700\text{ cm}^{-1}$  [Fig. 4(a)],  $1850$  and  $1150\text{ cm}^{-1}$  [Fig. 4(b)], and  $1170$  and  $580\text{ cm}^{-1}$  [Fig. 4(c)]. The evolution of the spectra corresponding to this resin alone was studied elsewhere [14]

and is shown for comparative purposes in Figs 5(a)–(c).

The evolution of the spectra in the zone between  $3200$  and  $2700\text{ cm}^{-1}$  is somewhat different in the case of the plastisol compared with the case of the resin:

—In the case of the resin [14], a gradual decrease of the bands at  $2970$  and  $2912\text{ cm}^{-1}$ , due to the C—H stretching of the  $\text{ClC—H}$  and methylene groups, was observed. In the residue at  $300^{\circ}$  these bands had almost disappeared and in the residue at  $330^{\circ}$  two shoulders, at  $2866$  and  $3050\text{ cm}^{-1}$ , and two more marked maxims, at  $3015$  and  $2928\text{ cm}^{-1}$ , appeared.

—In the case of the plastisol, there was an increase of the intensity in the region between  $3100$  and  $2800\text{ cm}^{-1}$ , whereas in the case of the resin a decrease was observed. Furthermore, the evolution of the shoulder at  $2866\text{ cm}^{-1}$ , as well as the disappearance of the two maxims at  $2912$  and  $2970\text{ cm}^{-1}$  and the appearance of the maximum at  $2928\text{ cm}^{-1}$  are highly marked. In addition, the band at  $3015\text{ cm}^{-1}$  grows more markedly than in the case of the resin. The band at  $2928\text{ cm}^{-1}$  must correspond to a characteristic structure of the residue of the PVC, whose evolution is clearly favoured by the presence of the plasticizer.

The changes of the spectra of the resin are gradual at temperatures above  $270^{\circ}$ , whereas in the case of the plastisols, between  $270$  and  $300^{\circ}$  the differences are small, but markedly increase their rate of change at temperatures higher than  $300^{\circ}$ . The bands at  $2912$  and  $2970\text{ cm}^{-1}$  may still be observable at  $309^{\circ}$  in the plastisol. The modifications of the structure of the polymer, responsible for these bands, are produced in the plastisol at temperatures somewhat higher than in the case of the resin, although they progress at a higher rate. Consequently, the plasticizer produces, initially, an apparent stabilizing effect, although in the latter stages the rate of the observed evolution of the spectra is higher. As a result, the overall effect may be a destabilizing effect, as observed in the TG experiments [3, 4].

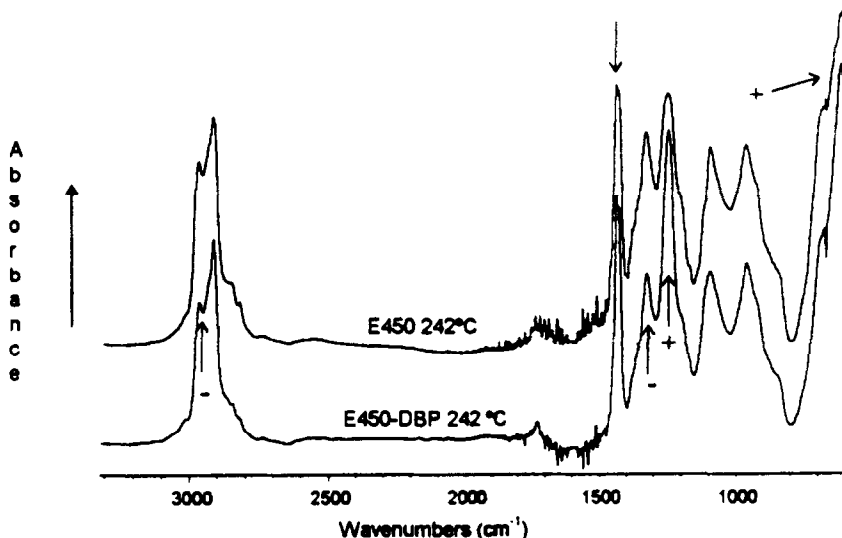


Fig. 3. Spectra of the resin E450 and the plastisol E450-65 phr of DBP at  $242^{\circ}$ .

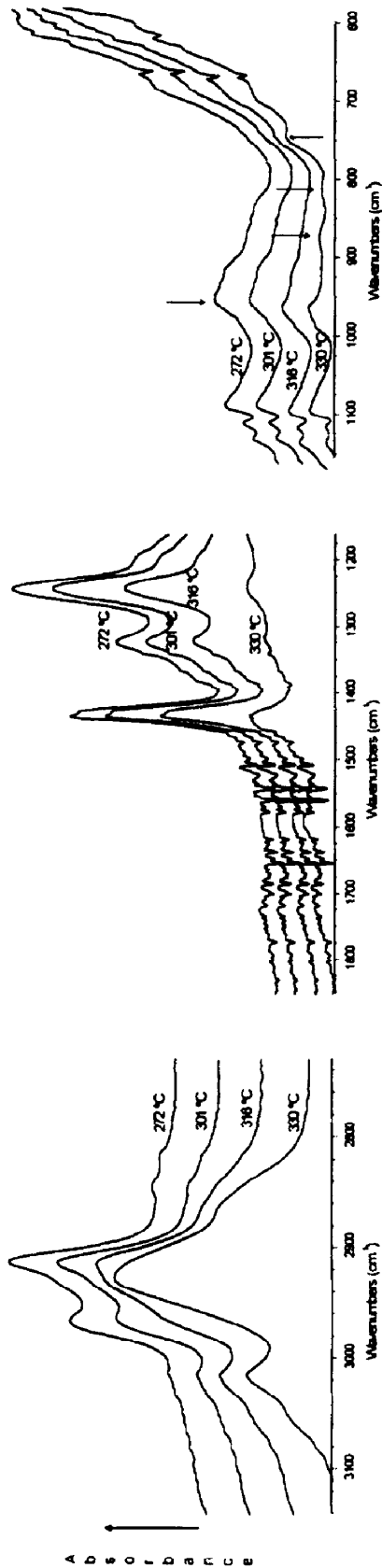


Fig. 4. Spectra of the plastisol E450-DBP 65 phr between (a) 3200 and 2700  $\text{cm}^{-1}$ , (b) 1900 and 1150  $\text{cm}^{-1}$ , and (c) 1170 and 580  $\text{cm}^{-1}$  at 272, 301, 316 and 330°.

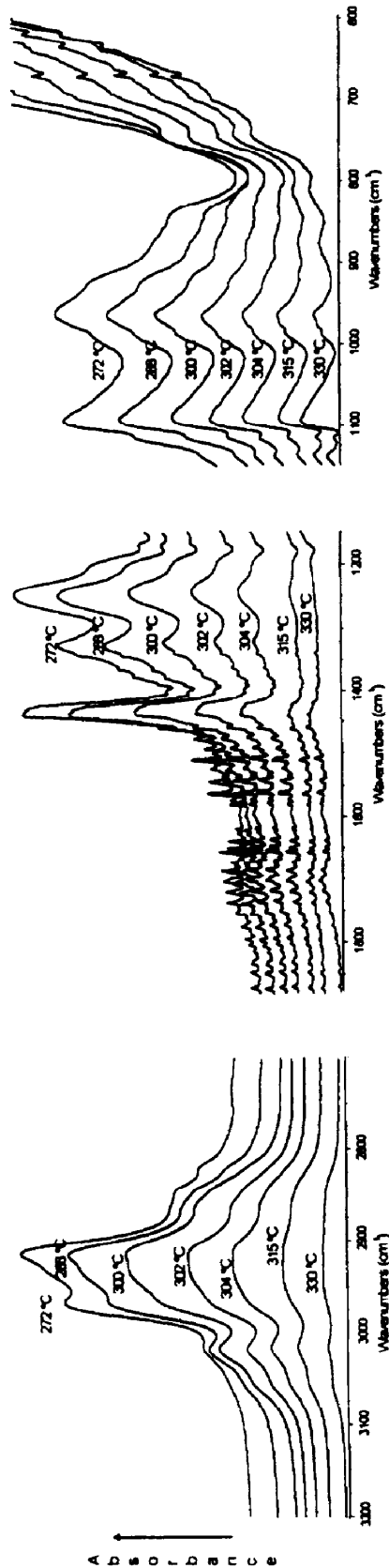


Fig. 5. Spectra of the resin E450 between (a) 3200 and 2700  $\text{cm}^{-1}$ , (b) 1850 and 1150  $\text{cm}^{-1}$ , and (c) 1170 and 580  $\text{cm}^{-1}$  at 272, 288, 300, 304, 315 and 330°.

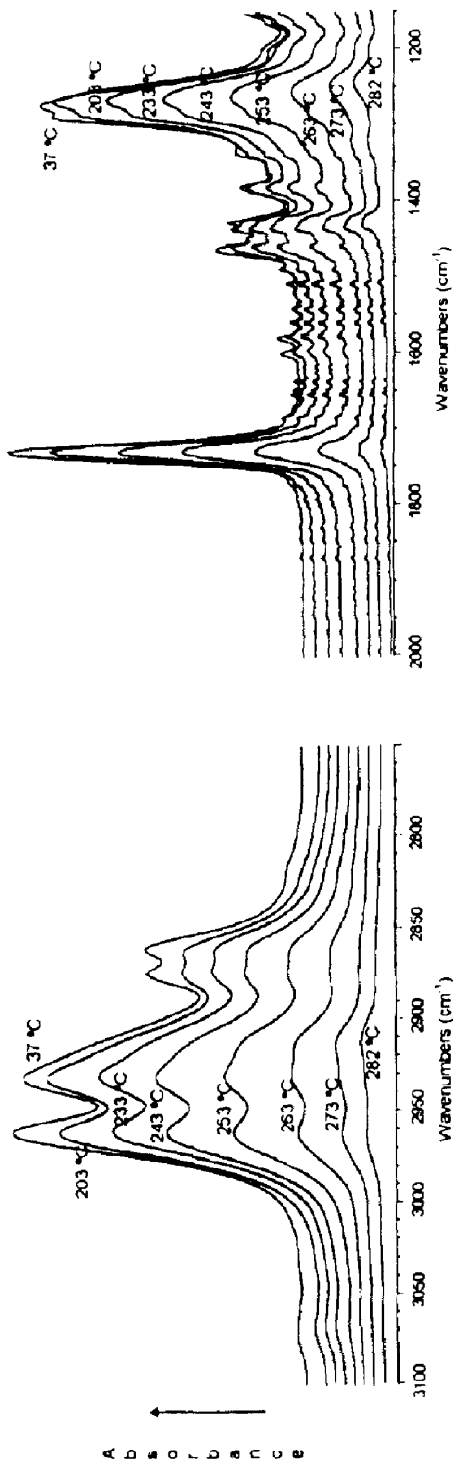


Fig. 6. Spectra of the plastisol E450-DOP 65 phr between (a) 3200 and 2700  $\text{cm}^{-1}$ , and (b) 2000 and 1150  $\text{cm}^{-1}$  at 37, 203, 233, 243, 253, 263, 273 and 282  $^{\circ}\text{C}$ .

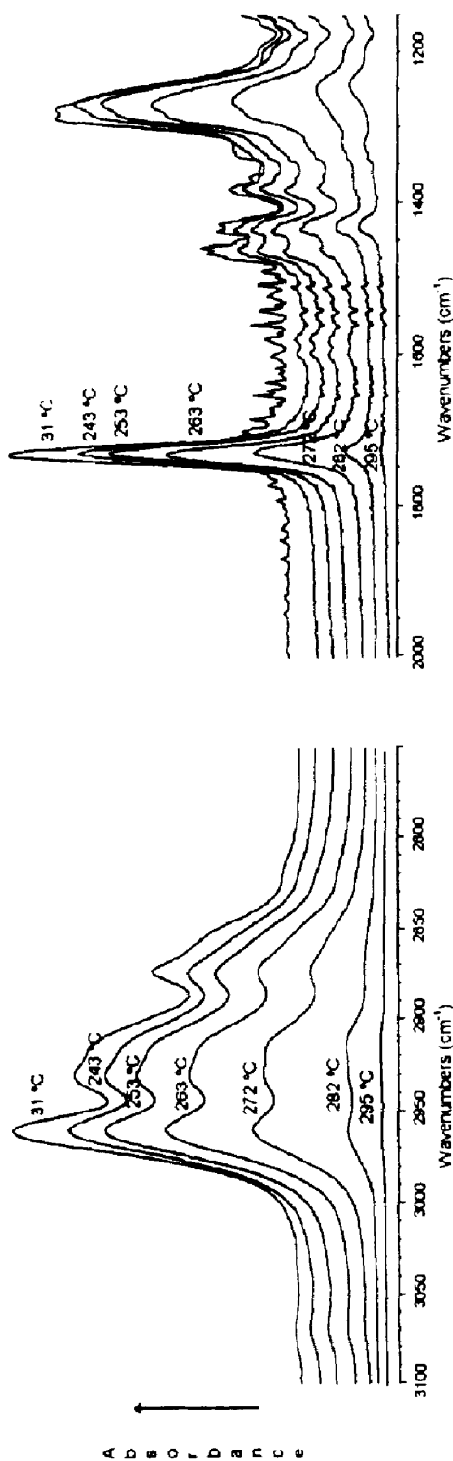


Fig. 7. Spectra of the plastisol E450-DIDP 65 phr between (a) 3200 and 2700  $\text{cm}^{-1}$ , and (b) 2000 and 1150  $\text{cm}^{-1}$  at 31, 243, 253, 263, 272, 282 and 295  $^{\circ}\text{C}$ .

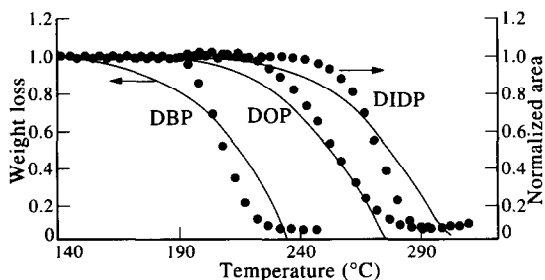


Fig. 8. Thermograms of the plastisols from E450 and 65 phr of DBP, DOP and DIDP (lines), and normalized area of the carbonyl band between 1820 and 1650  $\text{cm}^{-1}$  (symbols).

The next region of the spectrum considered, between 1900 and 1150  $\text{cm}^{-1}$ , is shown in Fig. 4(b). Several phenomena are observed: the appearance of a small band at 1595  $\text{cm}^{-1}$ , due to the presence of conjugated double bonds, the shift of the band at 1435  $\text{cm}^{-1}$  and the disappearance of two bands at 1330 and 1250  $\text{cm}^{-1}$ , due to the C—H stretching of ClC—H groups. These modifications were also observed in the spectra of the resins [Fig. 5(b)]. Nevertheless, and as in the previous region, these modifications occur not only at higher temperatures, but also at higher rates (i.e. within the 300–330° temperature range, in the case of the plastisol, compared with 270–330° in the case of the resins). At 330° these bands are still observable in the case of the plastisol, whereas in the case of the resin they were not apparent. Furthermore, the small band at 1900  $\text{cm}^{-1}$ , whose origin could be associated to structures of the type  $\text{C}=\text{C}=\text{C}-\text{H}$  [15], is not observed in the case of the plastisol.

In the residue of the resin at 330° [Fig. 5(c)], a band was observed at 966  $\text{cm}^{-1}$ , corresponding to stretching of double bonds *trans* substituted [15, 16], which is also clearly observed in the case of the plastisol

[Fig. 4(c)]. The bands at 875, 810 and 741  $\text{cm}^{-1}$ , observed in the case of the resin also appear in the case of the plastisol. It can also be observed in Fig. 4(c), despite the high drift of the base line, that the C—Cl band, between 600 and 700  $\text{cm}^{-1}$ , disappears.

### 3.2. Effect of the type of plasticizer

The behaviour of the plastisols from two other plasticizers of the phthalate family, DOP and DIDP, were also studied. The compatibility of the three plasticizers studied follows the sequence of their molecular weights, i.e.  $\text{DBP} > \text{DOP} > \text{DIDP}$ . Figures 6(a) and 6(b) show the evolution of the spectra of the plastisol with DOP at temperatures below 282° and in the regions 3100–2750 and 2000–1150  $\text{cm}^{-1}$ , respectively. Figures 7(a) and (b) show the corresponding spectra in the case of the plastisol of DIDP, at temperatures below 295°. The spectra in the region below 1150  $\text{cm}^{-1}$  are not shown, since they do not add any significant information to that already discussed.

Between 37 and 203°, there are very few differences observable in the plastisol of DOP. The intensive evolution of the plasticizer starts at around 233° and proceeds up to 282°, the temperature where the carbonyl band (at 1728  $\text{cm}^{-1}$ ) has completely disappeared, indicating the complete evaporation of the plasticizer. At this temperature the spectrum is very similar to that observed after the complete evaporation of the DBP. In the case of the DIDP the loss of the plasticizer starts, as expected, at higher temperatures [Figs 7(a) and (b)]. The main changes in these spectra start at around 253° and continue up to 295°, yielding a spectrum which is very similar to those obtained in the case of DBP and DOP after the complete evolution of the corresponding plasticizer. The temperature ranges where the evolution of the plasticizers occur agree with their boiling ranges and

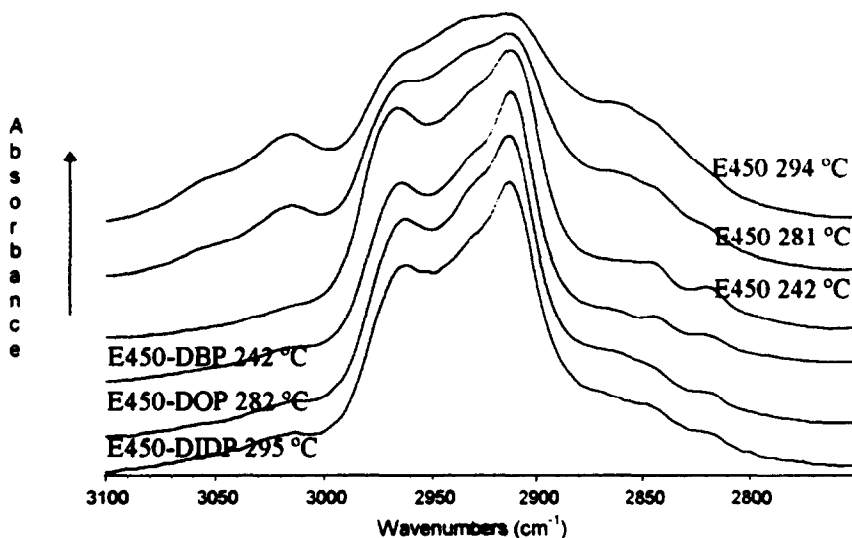


Fig. 9. Spectra of the plastisols from E450 and 65 phr of DBP at 242°, DOP at 282° and DIDP at 295° compared with the corresponding spectra of the resin E450 at 242, 281 and 294° between 3100 and 2750  $\text{cm}^{-1}$ .

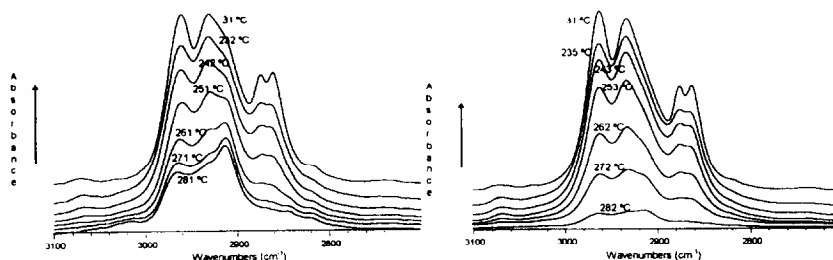


Fig. 10. (a) Spectra of the plastisol E450-DOP 40 phr at 31, 232, 242, 251, 261, 271 and 281°, and (b) spectra of the plastisol E450-DOP 90 phr at 31, 235, 243, 253, 262, 272 and 282°, between 3100 and 2700  $\text{cm}^{-1}$ .

molecular weights ordering. The differences observed with respect to the boiling ranges are due to the different pressures in both type of experiments.

Figure 8 shows the results of the thermogravimetric analysis corresponding to these plastisols at 10°/min. This figure also shows the normalized area under the carbonyl band (in the 1820–1650  $\text{cm}^{-1}$  range) in the dynamic IR experiments at the same heating rate. A good agreement is obtained for the range of evolution of the plasticizer by both techniques. Nevertheless, some differences are apparent. The temperature where the plasticizer evolution starts is somewhat higher when observed from the IR experiments, but this process proceeds at a lower rate, from the TG point of view. These differences may be due to diverse reasons, such as the following: the amount of sample is very different in both type of techniques, it is much higher in the case of TG, the thickness of the sample is also much higher in the TG experiments, the shape of the sample holder is also very different yielding different patterns of gas flows in both cases, the nature of the processes observed is different, although related, in both cases, to weight loss and absorption intensity variations, among others occur.

Once the plasticizer has been completely evaporated, the three residues present very similar spectra. This fact is curious, on considering the significant temperature difference (more than 50° between

DBP and DIDP). Figure 9 shows the residues for the three cases, once the corresponding plasticizer has been eliminated (i.e. when no carbonyl band is observed), together with the residue corresponding to the resin experiment at those temperatures. As already discussed, the three residues are very similar. The three plasticizers act in a similar way, delaying the temperature where the transformations of the spectrum in the zone between 3100 and 2700  $\text{cm}^{-1}$  start. Nevertheless, each plasticizer produces a distinct effect on the residue. The modification of the relative intensity of the bands cited previously is more marked in the case of the DBP, than in the case of the DOP, and this latter is more marked than in the case of the DIDP. The more compatible plasticizer interferes more markedly with the process of pyrolysis of the resin.

During the decomposition of the plastisols of DOP and DIDP at temperatures above 282 and 295°, respectively, the same changes already discussed in the case of the DBP plastisol can be observed.

### 3.3. Effect of the plasticizer concentration

As in the case of the effect of the type of plasticizer, in the case of the effect of the concentration there is some controversy in the literature. According to Milan and Braun [17] there is a minimum dehydrochlorination rate for a given concentration

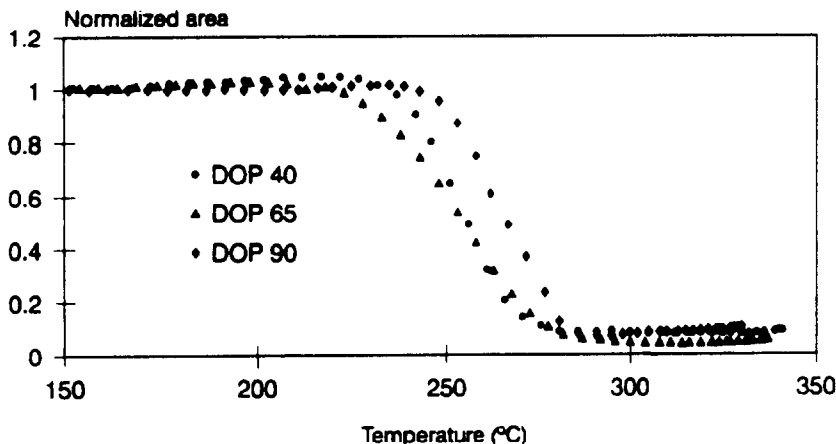


Fig. 11. Evolution of the normalized area of the band between 1820 and 1650  $\text{cm}^{-1}$  for the plastisols E450-DOP at 40, 65 and 90 phr.

of plasticizer, which is different for each type of plasticizer. This phenomenon is explained in terms of the interactions among the plasticizer and the polar groups of the resin that, at a certain concentration of plasticizer, can be stronger than those among the polymer chains. On the other hand, Minsker *et al.* [9] found that the thermal stability of PVC increases with the concentration of plasticizer at low concentrations and remains unaltered at high concentrations.

The effect of the concentration of DOP was studied in a range normally used in industrial applications of plastisols, i.e. 40, 65 and 90 phr. Figures 10(a) and (b) show the evolution of the spectra of the plastisols with 40 and 90 phr of DOP, at temperatures below 280° and in the region between 3100 and 2700  $\text{cm}^{-1}$ . All the spectra obtained, during all the stages considered, are very similar to those already presented. Figure 6(a) shows the same sequence of spectra for the plastisol with 65 phr. The spectrum of the plastisol with 90 phr, at room temperature, is more similar to that of the plasticizer, whereas in the spectrum of the plastisol with 40 phr of DOP, the band at 2912  $\text{cm}^{-1}$  due to the methylene groups of the resin and hardly observable in the other two formulations (especially in that with 90 phr) is clearly visible. These features are the logical consequence of the decrease of the concentration of plasticizer.

The bands corresponding to the plasticizer gradually disappear when the temperature is increased, as a consequence of its evaporation. Figure 11 shows the evolution of the area under the carbonyl band for the three plastisols. This process takes place in the same temperature range in the three cases. Only a slight delay is observed in the case of the plastisol with 90 phr of DOP.

The modifications of the spectra during the pyrolysis of the resin are shown in Figs 12(a) and (b), in the zone 3200–2700  $\text{cm}^{-1}$ , for the plastisols with 40 and 90 phr of DOP. At temperatures above 300°, the evolution of the spectra is slightly faster in the plastisols with higher amounts of plasticizer. The rest of the regions of the spectrum show very similar trends.

Figure 13 shows a clear relationship between the decrease of the normalized area of the carbonyl band, during its evaporation process, with the plasticizer concentration: the plastisol with less concentration of plasticizer is the one yielding a lower decrease in that area. Similarly, the increase of the area undergone by the residue is more marked for this plastisol (40 phr of DOP). Furthermore, a slight delay can be observed in the evaporation process for the plastisol with 90 phr of DOP. This figure also shows the temperature range where the minimum area is obtained. This can be observed as the area starts its increasing process at lower temperatures for the plastisols with less plasticizer. The evolution of this band starts later for the plastisol with 90 phr of DOP, but progresses faster. The behaviour of the plastisol with 40 phr of plasticizer is, as expected, more similar to the resin, clearly showing the effect of the concentration of plasticizer on the pyrolysis process of the resin.

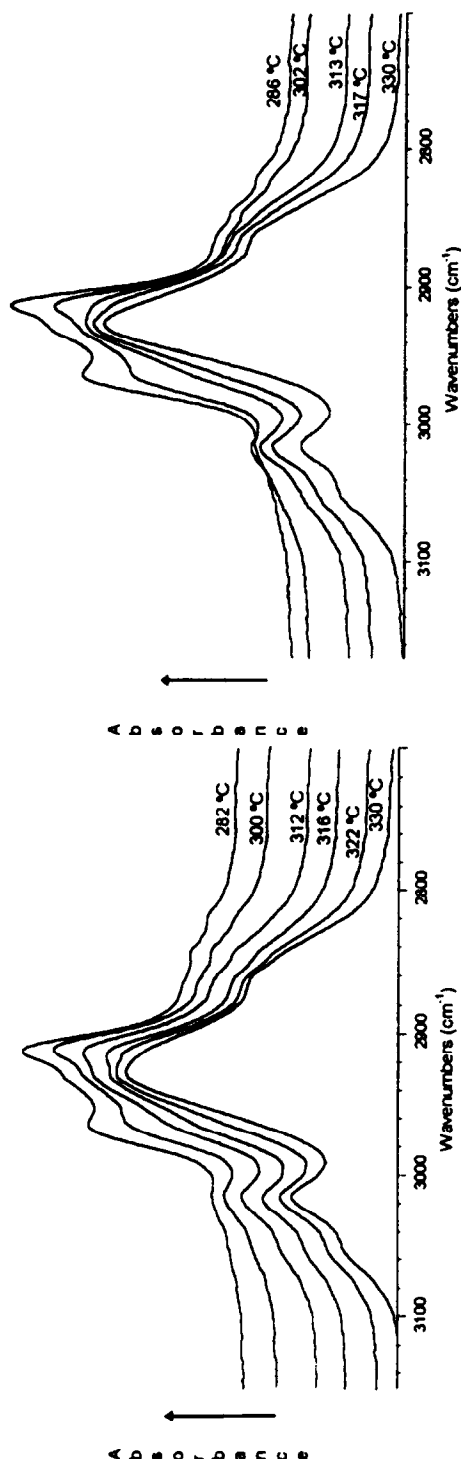


Fig. 12. (a) Spectra of the plastisol E450-DOP 40 phr at 282, 300, 312, 316, 322 and 330°, and (b) spectra of the plastisol E450-DOP 90 phr at 286, 302, 313, 317 and 330°, between 3100 and 2700  $\text{cm}^{-1}$ .

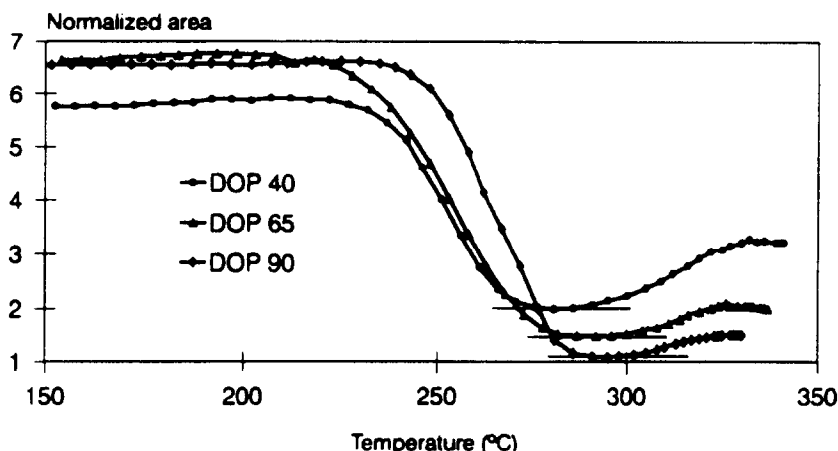


Fig. 13. Evolution of the normalized area of the band between 3120 and 2760  $\text{cm}^{-1}$  for the plastisols E450-DOP at 40, 65 and 90 phr.

#### 4. CONCLUSIONS

The first phenomenon occurring during the plastisols decomposition is the evaporation of the plasticizer, which leads to a spectrum very similar to that obtained for the resin at the same temperature. Each plasticizer evaporates at temperatures in good agreement with those obtained in plastisols by thermogravimetric analysis. After plasticizer evaporation, the pyrolysis of the resin is observable from the gradual disappearance of the bands related with the methylene groups and chlorine atoms and the appearance of small intensity bands corresponding to the stretching of C=C bonds of different origins. Similar small differences are observable in the intensity and position of these bands in the plastisols with respect to the case of the pyrolysis of the resins alone. The changes occurring in the plastisol during the pyrolysis of the resin are initially delayed, but above a certain temperature, they take place more markedly in the case of the plastisol. The effect is more marked for the more compatible plasticizer and for the more concentrated one.

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#### REFERENCES

1. Wypych, J., *Polyvinyl Chloride Stabilization*. Elsevier Science Publishers B.V., Amsterdam, 1986.
2. Kovacic, T., Velickovic, J., Cvorkov, L. and Ganbiroza, M., *Hem. Ind.* 1989, **43**(1), 1.
3. Marcilla, A. and Beltrán, M., *J. Vinyl Add. Tech.* 1995, **1**(1), 15.
4. Marcilla, A. and Beltrán, M., *Polym. Deg. Stab.*, 1996, **53**, 261.
5. Wypych, J., *Polyvinyl Chloride Degradation*. Elsevier Science Publishers B.V., Amsterdam, 1985.
6. Moskala, E. J. and Lee, D. W., *Polym. Deg. Stab.* 1989, **25**, 11.
7. Millán, J., Martínez, G., Jimeno, M. L., Tiemblo, P., Mijangos, C. and Gómez-Elvira, J. M., *Makromol. Chem., Makromol. Symp.* 1991, **48/49**, 403.
8. Minsker, K. S., Abdullin, M. I. and Ableev, R. I., *Vysokmol. Soedin., Ser. A* 1987, **29**(4), 768.
9. Minsker, K. S., Kolesov, S. V. and Zaikov, G. E., *Degradation and Stabilization of Vinyl Based Polymers*. Pergamon Press, Oxford, 1988.
10. Abdullin, M. I., Ableev, R. I., Yanboisov, V. M. and Minsker, K. S., *Polym. Sci. U.S.S.R.* 1988, **30**(4), 749.
11. Kovacic, T., Mrklic, Z., Roje, U. and Klaric, Y., *Polimeri* 1986, **7**(4–5), 105.
12. Marcilla, A., Beltrán, M., García, J. C. and Mang, D., *J. Vinyl Add. Tech.* 1995, **1**(1), 10.
13. Beltrán, M., Marcilla, A. and García, J. C., *Eur. Polym. J.* 1997, **33**, 453.
14. Beltrán, M. and Marcilla, A., *Eur. Polym. J.* Accepted.
15. Pretsch, E., Clerc, T., Seibl, J. and Simon, W., *Tablas para la elucidación estructural de compuestos orgánicos por métodos espectroscópicos*. Alhambra, Madrid, 1989.
16. Oakes, W. G. and Richards, R. B., *J. Chem. Soc.* 1949, 2929.
17. Milan, I. and Braun, D., *Angew. Makromol. Chem.* 1969, **9**, 186.