

Influence of Crystallinity in the Curing Mechanism of PVC Plastisols

J. López,¹ R. Balart,¹ A. Jiménez²

¹Mechanical and Materials Engineering Department, Polytechnic University of Valencia, Alcoy, Alicante, Spain

²Analytical Chemistry Department, University of Alicante, Alicante, Spain

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ABSTRACT: The influence of the crystalline areas observed in poly(vinyl chloride) (PVC) the mechanical and thermal properties of PVC plastisols was studied. Several industrial-degree PVC resins were used to obtain a broad range of molecular weights and processing conditions for PVC plastisols. The gelation process was fully studied at different temperatures and was related to the existence of crystalline areas at high temperatures, even near the glass transition. A simple explanation of the phenomena observed during the gelation of plasticized PVC is proposed, according to the variation in the mechanical and thermal properties

at different temperatures. The final gelation was obtained at 140–150°C, which was a lower temperature than those at the beginning of the thermal degradation process. The thermodynamic aspects of the gelation of plasticized PVC were mainly controlled by the PVC resin properties, whereas the plasticizer only influenced the diffusion and stability of the material. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 538–544, 2004

Key words: poly(vinyl chloride) (PVC); gelation; mechanical properties; thermal properties

INTRODUCTION

Although the measurement of crystallinity in poly(vinyl chloride) (PVC) presents some difficulties, such as the small number of clearly crystalline areas, it is well known that some of these areas can be found in its structure. Despite crystallinity increases with syndiotacticity, a particular behavior is often observed. Both thermal analysis and X-ray diffraction (XRD) have provided evidence for the atypical crystalline nature of PVC.¹ Measurements made with small-angle neutron scattering have also confirmed the presence of poorly defined crystallinity in PVC.²

One industrial application of PVC is the use of plastisols, which are formed by blends of a PVC resin and additives, mainly plasticizers, which can be used in amounts as high as 30 wt % or even higher. The gelation of a PVC plastisol is an irreversible process in which a liquid dispersion of a PVC resin with a plasticizer becomes a solid material with elastomeric properties when the temperature increases. If plasticized PVC is not fully gelled, the optimum physical properties of the material cannot be attained. The full development of the physical properties, such as tensile strength and elongation at break, is dependent on both temperature and time. If the gelling temperature is not high enough, the optimum physical properties will

never be achieved, no matter how long the system is held at that temperature.

Crystallinity has been detected in plasticized PVC and can be used to explain its exceptionally useful range of mechanical properties. The existence of a three-dimensional gel structure, which prevents the occurrence of irrecoverable viscous flow has been proposed.¹ It has also been proposed that plasticized PVC could be considered a simple two-phase system consisting of rigid crystallites and a flexible amorphous phase.³ Thermal and thermomechanical analysis have been used to investigate the thermal transitions in crosslinked plasticized PVC.⁴ The formation of a physical network complementary to the chemical network increased the melting temperature and other properties of the material. Those physical gels could be formed from crystalline polymer solutions and could induce variation in the network structure and physical properties of the gel. Hong and Chen recently proposed the existence of a small junction point for the formation of microcrystals in PVC formulations.⁵ The same authors indicated that the crystallinity of a dried gel is very low and does not represent any variation in some properties, such as elasticity, but in the case of a wet gel, crystallinity varies significantly, inducing some changes in elasticity and the glass-transition temperature (T_g).⁶ It proposed that two types of microcrystals were present in the gel structure: primary microcrystals in the virgin powder and secondary and fringed micellar microcrystals from melts or solutions.⁷ The secondary structure forms when the plastisol melts are cooled or the solutions are gelled. Those

Correspondence to: A. Jiménez (alfjimenez@ua.es).

two structures exert a major effect on the rheological and mechanical properties.

The effect of plasticizers on PVC and the mechanisms that modify its properties from the liquid state (plastisol) to the solid state (cured) have been studied by many researchers,⁸⁻²² due mainly to the industrial importance of this process. It is well known that viscosity is one of the main parameters to be controlled during gelation. The presence of the solid phase increases the viscosity of the plasticizer. As the plastisol is heated, there is a diffusion of plasticizer into the resin particles, increasing their size and decreasing the relative amount of free plasticizer. Most of these works have focused on the determination of the plasticization mechanism, and the temperatures for different stages of this process have been calculated. Some techniques, such as rheological techniques, mechanical strength measurements, and test tube methods for the determination of the processing conditions of a plasticized PVC gel, were developed to study this process. Due to the use of these different techniques, a great dispersion in results has been found, but some general features can be concluded. There are important changes in the plastisol around 80–100 and 160–190°C. This agrees with industrial practice on the transformation of PVC plastisols. There is a temperature interval around 100°C where a pregelation process takes place. In this stage, a solid material is produced that is characterized by characterized low mechanical properties, which makes the material useless for industrial application. The temperature must be at least 160°C for one to obtain pieces with the appropriate mechanical properties. Below this temperature, even with long curing times, one cannot obtain well-cured pieces.

The presence of these two temperature intervals is very useful in the knowledge of the curing process of a PVC plastisol. We can also relate them to the structure of PVC. The first interval, around 80–100°C, is coincident with the PVC T_g . Therefore, it is supposed that when the T_g is reached, an opening of the chains due to an increase in mobility is produced. This marks the interaction between the plasticizer and the PVC resin.

With regard to the second temperature interval (160–180°C), some authors have indicated that PVC is not a completely amorphous–glassy material.^{1,7,23} This affirmation has been based on electronic microscopy and measurements. The proposal of a secondary crystallinity could justify the observation of a second stage in the gelation process due to the breaking of the primary crystalline structure. This would permit complete interaction between the PVC resin and the plasticizer. In many cases, processing above 190–200°C causes a small increase in crystallinity. This secondary network has previously been studied by XRD and other expensive and complicated techniques.²³ As the

TABLE I
Characteristics of the PVC Resins Used in This Work

Resin	Manufacturer	Application	K
Etinox 450	Aiscondel		67
Hispavic 2950	Solvay		68
Hispavic 367	Solvay		67
Solvic 367	Solvay		67
Solvic 373 MG	Solvay		73
Vestolit 7010	Huls	Plastisols and Foams	70
Vestolit 7021	Huls	Plastisols	72
Vestolit 7021 (2)	Huls	Plastisols	72
Vestolit P-1353-K	Huls	Rotomolding	70
Vestolit P-1403-K	Huls	Rotomolding	70
Vicir K70		Injection	70
PVC pellets		Injection	
PVC screening II		Injection	
PVC screening III		Injection	

increase in crystallinity at higher temperatures is much more important, thermal analysis can be a useful tool for carrying out crystallinity studies on PVC plastisols. Differential scanning calorimetry (DSC) has been proposed for the measurement of crystallinity in polymers, and a recent review highlights this possibility.²⁴ However, the inherent problem in all DSC measurements is the concurrent recrystallization and melting of the polymer sample on heating to the temperature where the degradation of PVC plastisols is observed. Thermogravimetric analysis (TGA) can be used to study the degradation process and to avoid the complication caused by this high-temperature process. The main aim of this study was to examine the influence of crystallinity in the curing mechanism of PVC plastisols studied by DSC. We also measured the mechanical properties of some particular PVC plastisols.

EXPERIMENTAL

Materials

Several different commercial PVC resins were used in this study to cover a broad range of conditions and resin properties. A summary of the main characteristics of each resin is presented in Table I. The Fikentcher constant (K) was calculated by means of the determination of viscosities as carried out by the application of the DIN 53-726 standard. As is well known, this parameter is directly related to the average molecular weight of the resin. The main part of this study was carried out by with Vestolit 7021 (Huls, Germany) as the PVC raw material. Our group characterized this resin in previous works.^{25,26}

Industrial grade diethylhexyl phthalate (DEHP) was selected as the main plasticizer for the preparation of plastisols. This plasticizer has historically been the

most used in the preparation of PVC plastisols because of its good properties and low costs. The purity of DEHP was checked with gas chromatography (Shimadzu GC-9A, Kyoto, Japan) with the observation of a single peak, which meant the degree of purity was high enough to use this plasticizer.

Plastisols were prepared by the mixture of adequate amounts of resin and plasticizer in a Brabender P-600 mixer for 20 min at $23 \pm 2^\circ\text{C}$. The paste obtained was then put in a vacuum dryer ($P < \times 10^2 \text{ Pa}$) for 5 min. Once the air was eliminated from pastes, they were ready for the curing process, which was carried out in a ventilated oven at the specified conditions.

Equipment and procedure

The determination of the mechanical properties was carried out with a universal testing machine (Ibertest Elib 500); which was able to determine the tensile strength, elongation at break, and modulus in a single experiment. Samples were used with no prior treatment, and probes were prepared with an adequate tool to get the final standard form ($4 \times 8 \text{ mm}$ rectangular samples specially prepared for the test). Shore A hardness measurements were carried out with a Baxlo durometer, with the use of samples 3 mm thick according to the Spanish standard UNE-53-130.

DSC measurements were carried out with a differential scanning calorimeter (Mettler Toledo DSC821, Greinfensee, Switzerland), which was able to perform runs from -50 to 500°C . Runs were carried out in a nitrogen atmosphere from room temperature to 250°C , as we believed that this temperature was high enough to be considered the beginning of the degradation process.

Dynamic degradation measurements were performed with a Mettler-Toledo TGA-SDTA 851e instrument, which allowed heating rates from 1 to $200^\circ\text{C}/\text{min}$ up to a temperature of 1200°C . Dynamic tests were run from 30 to 900°C at different heating rates between 5 and $30^\circ\text{C}/\text{min}$ at $5^\circ\text{C}/\text{min}$ intervals. This

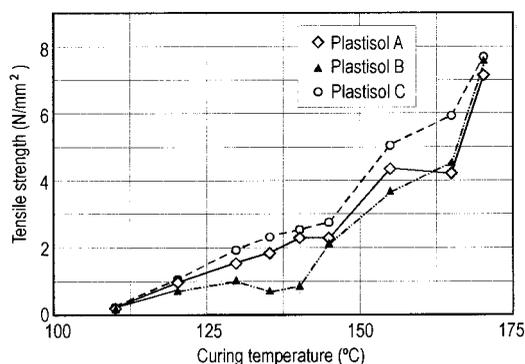


Figure 1 Variation of tensile strength with curing temperature for different PVC plastisols.

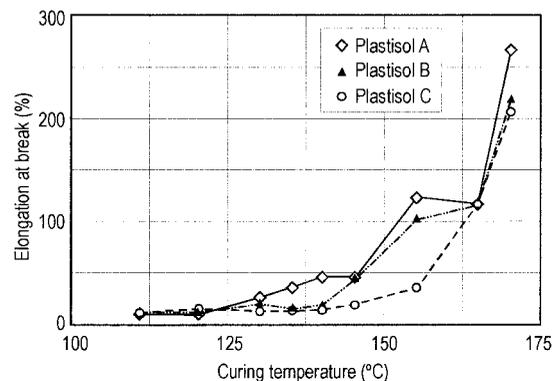


Figure 2 Variation of elongation at break with curing temperature for different PVC plastisols.

procedure was selected to cover the whole degradation process of PVC, although we were only interested in the first stage, that is, dehydrochlorination. TGA tests were performed in alumina crucibles, where samples were placed without any previous treatment and experiments were run immediately. TGA tests were carried out in a nitrogen environment at a flow rate of $200 \text{ mL}/\text{min}$ to remove all of the corrosive gases evolved during the degradation and to avoid thermoxidative degradation.

RESULTS AND DISCUSSION

Mechanical properties: influence of the curing temperature

One of the best ways to follow the evolution of the curing process of a plastisol is to determine the mechanical properties of the different formulations and gelation states. Three formulations of plastisol with the same composition (100:70 PVC:DEHP) were prepared as indicated in the Experimental section and were further cured at different temperatures in the range 110 – 180°C for 5 min. Once cured, the influence of the curing temperature on the samples' mechanical properties, tensile strength, and elongation at break was determined. The results for the tensile strength are presented in Figure 1. As observed, the values obtained were similar to those previously reported.²⁵ The tensile strength increased with cure temperature, but the slopes were different before and after 150°C . In the first stage (temperature range- 100 – 150°C), the solid did not have enough cohesion, and the values increased slowly. The gel had not solidified completely, and therefore, the increase in tensile strength was low. Temperatures above 150°C marked the complete cure of the plastisol. Therefore, the tensile strength improved more quickly, reaching the higher results at 180°C . Similar results were obtained for the elongation at break, as shown in Figure 2. As ex-

pected, the results indicated an increase in material cohesion as we used higher curing temperatures.

The hardness (shore A) results for the same samples are presented in Figure 3. The results were not as expected as in the case of the other mechanical properties. There was not a continuous increase, but a maximum was reached at approximately 140°C with a further decrease for higher curing temperatures. A possible explanation for this could be obtained by a consideration of the nature of the test. When we determine hardness by means of the shore A method (based on a needle penetration), we are measuring the opposition of the material to be deformed, which is related to its rigidity and, cohesive forces, which are related to the break strength. Therefore, we found a first stage in which the hardness increased with cure temperature, which was caused by an increase in the material cohesion. At temperatures above 140°C, the hardness decreased with cure temperature. Although we know by the tensile strength measurements that the molecular cohesion was continuously increasing, an important decrease in the rigidity should be considered in the plastisol structure at high cure temperatures, which caused the observed decrease in hardness. A possible justification to this decrease in rigidity of the plastisol can be proposed if we consider that PVC polymeric chains form microcrystalline areas that break when temperatures higher than 150°C are reached. As this behavior at higher cure temperatures was not observed in the case of rigid PVC, we concluded that these microcrystalline areas were not formed once the gelation process was finished. This phenomenon was also observed with other *o*-phthalic esters used as plasticizers, such as diisononyl phthalate, and for different concentrations of them, as shown in Figure 4. In this case, it was the same interval (140–150°C) that marked an inflection point and an important change in properties.

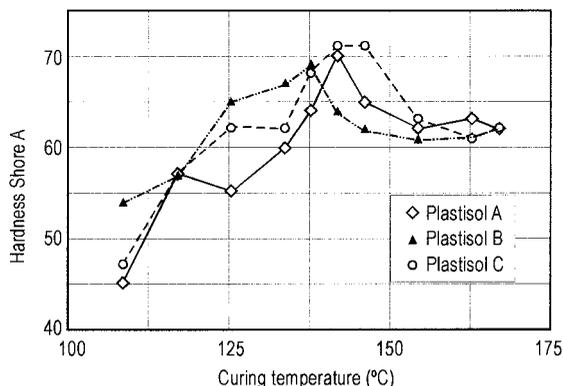


Figure 3 Variation of hardness (shore A) with curing temperature for different PVC plastisols.

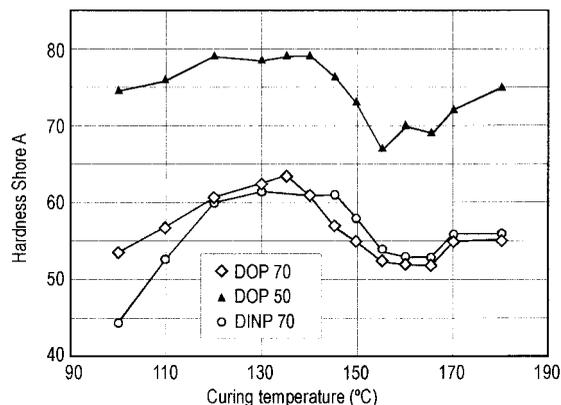


Figure 4 Variation of hardness (shore A) with curing temperature for different PVC plastisol formulations and different plasticizers.

Mechanical properties: influence of curing time

To correlate the mechanical properties with the influence of curing time in the plastisol gelation, a similar study for different curing times between 2 and 30 min at two different temperatures was carried out. The selection of temperatures was made on the basis of the two stages in the mechanism previously indicated, with a temperature lower and an other higher than 150°C (130 and 180°C, respectively). The variation of tensile strength versus time is shown in Figure 5.

It seemed that times higher than 15 min did not represent any improvement in the tensile strength of PVC plastisols, even at low temperatures, such as 130°C. Similar results were obtained for the elongation at break and hardness. Therefore, these results indicate that a minimum temperature of 150°C and time 15 min were needed for an appropriate curing process of the PVC plastisol.

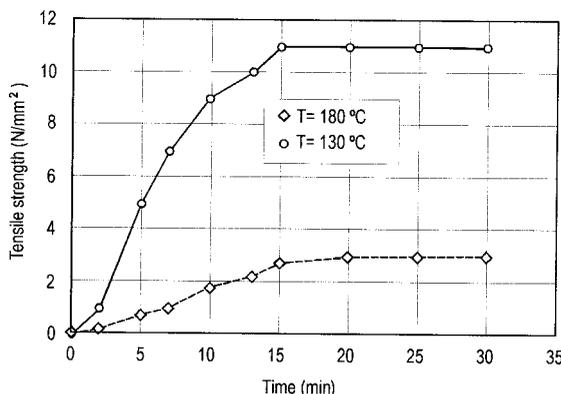


Figure 5 Variation of tensile strength with curing time of different PVC plastisols (PVC DOP: 100:70) at two different temperatures.

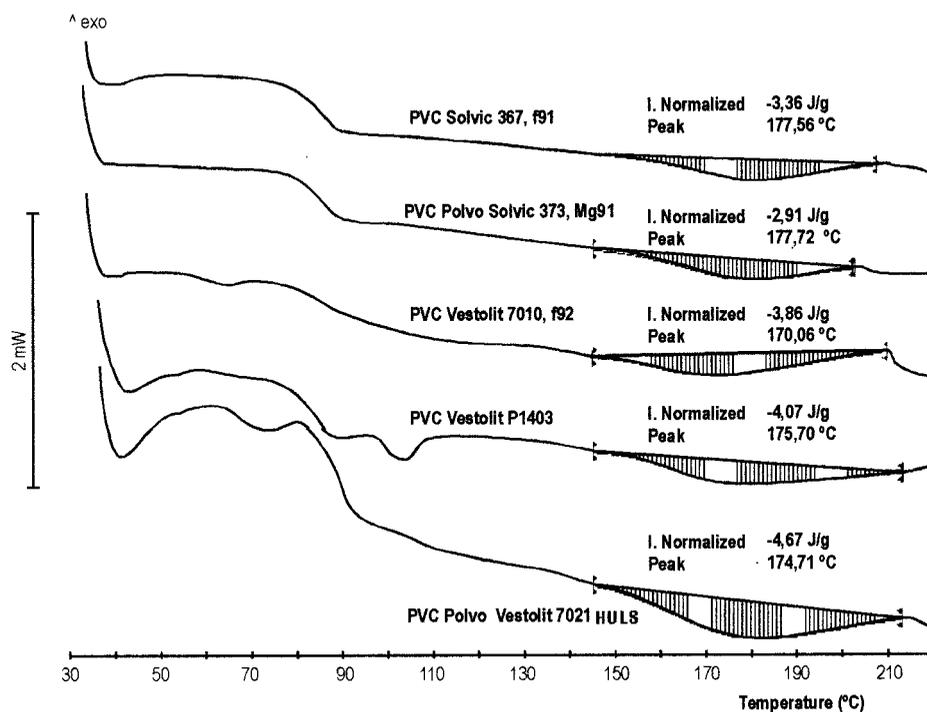


Figure 6 DSC curves of different PVC resins.

Thermal analysis

As is well known, the degree of crystallinity of a polymer is dependent on temperature.²⁴ Many of the phenomena related to the internal structure of the polymer, such as crystallization, annealing, melting, and recrystallization, occur during the heating of the sample. In the case of PVC, it is possible to obtain information by means of thermal analysis techniques, such as DSC and TGA. To study the small changes in crystallinity with temperature in PVC, several temperature scans were carried out for the different PVC samples indicated in the Experimental section. The main results of this study are presented in Figure 6. As shown, the DSC curves of PVC resins showed a first step related to the glass transition around the tabulated T_g value of the standard PVC resin (81.4°C). The small differences observed in this first step could be attributed to the different compositions of the industrial resins used in this study.

A second transition in the DSC curves was observed with a broad endothermic peak in the interval between 160 and 200°C. This broad peak was observed for each of the resins studied in this work, with associated energies varying from 2 to 6 J/g, as indicated in Table II. This isolated result would not be very significant due partly to its proximity to the beginning of the thermal degradation of the plastisol. This peak could be related to the melting of small crystalline areas in the PVC plastisol after gelation, which could explain some of the previously mentioned mechanical

properties. However, the thermal degradation of the PVC resins (not plasticized) started at temperatures in the same range; therefore, the contribution of this important phenomenon at high temperatures should be also considered.

This small endothermic peak was observed for all of the PVC samples, independently of their molecular weight and the foreseen processing technique in its use (injection, rotomolding, etc). However, this peak was not detected in plasticized PVC, as shown in Figure 7. As previously indicated, one of the possibil-

TABLE II
Energies Associated to the Second Peak of the DSC Curves of Different PVC Resins

Resin	Energy (J/g)	Standard deviation
Etinox 450	2.3	0.3
Hispanic 2950	4.3	0.9
Hispanic 367	3.9	0.6
Solvic 367	3.4	0.9
Solvic 373 MG	2.9	0.5
Vestolit 7010	3.9	0.4
Vestolit 7021	2.9	0.7
Vestolit 7021 (2)	4.7	0.6
Vestolit P-1353-K	5.3	0.9
Vestolit P-1403-K	5.8	0.5
Vicir K70	3.1	0.8
PVC pellets	3.4	0.6
PVC screening II	4.7	0.6

The results are based on three replicated tests.

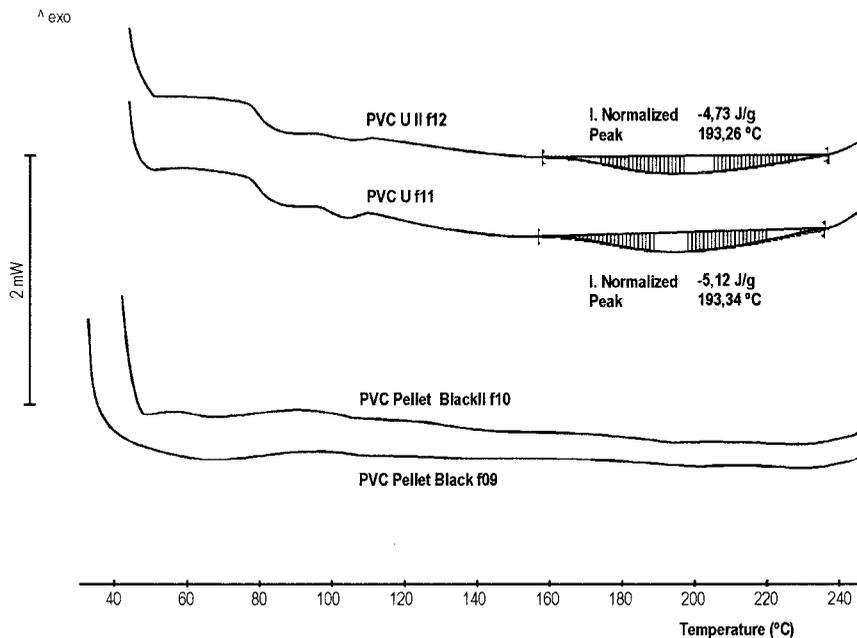


Figure 7 DSC curves of some unplasticized and plasticized PVC samples.

ities for the presence of this second peak in the DSC curves was related to the beginning of the thermal degradation. However, TGA analysis showed that decomposition of the polymer still had not begun in the temperature range here considered, as shown in Figure 8.

CONCLUSIONS

In the thermal analysis of the curing process of PVC plastisols, two temperature intervals were observed. The first one, coincident with the T_g of the polymer, was observed at 80–90°C, where a gel with insufficient cohesion to be worked with was obtained. This is known as the pregel state. The complete curing of the material was observed when the temperature interval 140–150°C was passed. This process was followed by

DSC with a small but significant endothermic transition not related to the thermal degradation of PVC, which started at higher temperatures. Therefore, this transition could have been due to a structural change in the material and the beginning of a melting process.

The assignment of curing temperatures to structural changes in PVC allows one to explain in a simple way the plasticization process when a PVC resin and a plasticizer are mixed. In the liquid plastisol (at room temperature), some molecules of plasticizer remain on the surface of the PVC macromolecular chains without mixing. Polymeric chains present higher mobility at temperatures near the T_g (first temperature interval), and plasticizer molecules are easier diffused between chains. If the process is stopped and the gel is cooled, we obtain a solid without cohesion but with a high hardness in some areas. This may be due to the partial plasticization, with areas of rigid PVC not accessible to the plasticizer still remaining in the material structure.

To produce a homogeneous and useful plasticized PVC, it is necessary to permit the total diffusion of plasticizer into the polymeric chain and to break the rigid and crystalline areas. This process was observed at approximately 140–150°C, and the plasticizer was able to mix completely with the PVC resin. Therefore, when cooling, we obtained a flexible solid with no crystallinity, a lower hardness, and a higher cohesion (tensile strength and elongation at break).

This model of plasticization indicates that the thermodynamic aspects of the process are dependent on the PVC structure, T_g , and crystallinity, which is variable according to the molecular weight and manufac-

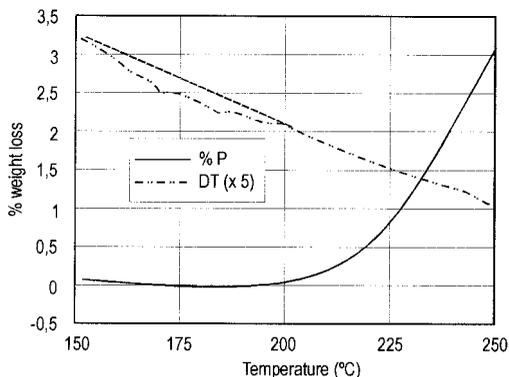


Figure 8 TGA analysis of plasticized PVC.

turing of the resin. The plasticizer only has influence in the dynamic aspects of the curing process (diffusion) and in the stability of the plastisol (migration).

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