

# Hydrothermic Aging of Plasticized Poly(vinyl chloride): Its Effect on the Dielectric, Thermal, and Mechanical Properties

H. Djidjelli,<sup>1</sup> M. Kaci,<sup>1</sup> A. Boukerrou,<sup>1</sup> D. Benachour,<sup>2</sup> J. J. Martinez-Vega<sup>3</sup>

<sup>1</sup>Laboratoire des Matériaux Organiques, Université A. Mira, Béjaia, Algeria

<sup>2</sup>Laboratoire de Génie des Polymères, Université F. Abbas, Sétif, Algeria

<sup>3</sup>Laboratoire de Génie Électrique, Université Paul Sabatier, Toulouse, France

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**ABSTRACT:** Accelerated hydrolytic aging (according to the NFT 5166 method) was performed on samples of poly(vinyl chloride) (PVC) plasticized with dioctylphthalate (DOP) and dinonyladipate (DNA) at different concentration ratios. The aging test consisted of immersing the samples in boiling water at 100°C. The samples were removed from water regularly, that is, every 2 h, for mechanical, thermal, and dielectric characterizations. Thermograms of PVC plasticized with DOP revealed no migration of the plasticizer independent of the concentration used. Moreover, the thermal stability of the samples was not affected by the hydrothermal aging. However, for PVC samples plasticized with DNA, a small amount of the plasticizer migrated from the polymer matrix with a considerable effect on the thermal stability. In fact, the data indicated a decrease in the decomposition temperature from 275 to 225°C, particularly for

samples containing 50% (w/w) DNA immersed up to 10 h. The mechanical results showed that for a plasticizer content greater than 30% (w/w), the strain at break obtained for samples plasticized with DNA was lower than that for samples plasticized with DOP because the DNA molecules were more likely to be removed by water on account of their polarity and dimension. Finally, the dielectric measurements showed that the permittivity of all the PVC samples plasticized with DOP and immersed in boiling water was higher than that of the virgin samples. On the contrary, the permittivity of the aged unplasticized PVC was less than that of the nonimmersed samples. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3447–3457, 2003

**Key words:** poly(vinyl chloride) (PVC); aging; thermogravimetric analysis (TGA)

## INTRODUCTION

Like all materials, polymers used for electrical cables are subjected to aging, which leads to a deterioration of their properties during use. The aging effects induced in a material, on the macroscopic scale, are cracks, which result in the loss of the isolation property. Aging is due to several factors, including the temperature (external or joule effect), electrical field intensity, moisture, and pollution. The loss of the isolation property is often due to some physicochemical property changes (e.g., mechanical, thermal, and dielectric).

Studying the hydrolytic aging of poly(vinyl chloride) (PVC) is necessary because electrical cables are, in many cases, in contact with water. Although literature dealing with the hydrolytic aging of polyesters and polyamides is available,<sup>1–3</sup> published data for thermoplastics are quite scarce.<sup>4</sup> Hydrolytic aging may be defined as the absorption by the polymer of a certain amount of water, the migration of additives, and some chemical reactions (hydrolysis reactions).

These reactions induce chain scissions resulting in molecular weight reduction and an embrittlement of the material. Hydrolysis effects can be associated with physical interactions between the polymer and water.

This study dealt with the effects of water on the mechanical and thermal properties of PVC formulated with two different plasticizers, dioctylphthalate (DOP) and dinonyladipate (DNA), at different contents (0, 10, 20, 30, 40, and 50 wt %). The choice of the DNA plasticizer was interesting because DNA is nontoxic and less viscous than DOP, which is commonly used in the PVC industry.

## EXPERIMENTAL

### Materials

The formulations used were based on PVC, produced by the Algerian company ENIP, with the following physical characteristics: grade = 4000 M,  $k_{\text{wert}} = 65–67$ , density = 0.48–0.56 (powder PVC), and thermal stability = 60 min (according to ISO Method 182-2).<sup>5</sup>

The other ingredients added to the PVC resin were DOP, with a viscosity of 80 MPa s and a molecular weight of 390 g/mol; DNA, with a viscosity of 19 MPa s and a molecular weight of 396 g/mol; Ba–Cd–Zn,

Correspondence to: H. Djidjelli (hocine@lget.ups-tlse.fr).

**TABLE I**  
**Mass Composition of the Formulations**

	Ratio of plasticizer (% w/w)					
	0	10	20	30	40	50
DOP	F0	F10P	F20P	F30P	F40P	F50P
DNA	F0	F10A	F20A	F30A	F40A	F50A

F = formulation;  $x$  = plasticizer ratio; P = phthalate plasticizer (DOP); A = adipate plasticizer (DNA);  $y$  = aging time in hours; F0 = unplasticized PVC;  $ty$  = aging time in hours for the unplasticized PVC.

based on carboxylates and used as a thermal stabilizer; soya oil, used as an internal lubricant; and stearic acid, used as an external lubricant.

### Preparation of the blends

For the study of the mechanical, dielectric, and thermal behavior of plasticized PVC in water at 100°C, two types of samples were prepared, one for each plasticizer content. Five different contents were used. Therefore, 10 different formulations were prepared in addition to the nonplasticized one. All the formulations were coded according to Table I. The nonplasticized formulation was F0. The different compounds were obtained with a double-wall steel mixer. The rotation speed was equal to 3000 rpm/min. The temperature was about 50°C (so that gel formation would be avoided). The dry blends obtained were used for the film preparation, having a thickness of 0.33 mm from a calendaring process. The operating conditions were fixed at 170°C for a residence time of 7 min. The normalized samples were cut for the different characterization tests. The unplasticized samples (F0) and those with low plasticizer concentrations (F10P, F10A, and F20P) were brittle, so it was practically impossible to prepare samples for mechanical characterization and other analyses.

### Hydrolytic aging of the samples

The accelerated hydrolytic aging of the samples of the different formulations was performed according to the French norm NFT 5166 based on sample immersion in water at 100°C. The experiments were carried out in a thermoregulated bath. The specimens were periodically removed (every 2 h), and the maximum immersion period was 9 h.

### Characterization apparatus

The sample weights before and after the samples were aged in water were used for the calculation of the weight variation. The calculations were determined with a high-precision analytical balance (0.01%). The weight variation could be attributed to three phenomena occurring simultaneously:

Plasticizer loss (physical process).

PVC thermal aging due to dehydrochlorination (chemical process).

Eventual water absorption.

A thermogravimetric method was used mainly for two purposes. The first was the determination of the onset temperature of decomposition of the samples before exposure so that the effect of the nature and concentration ratio of the plasticizer on the thermal stability could be measured. The second was to separate the aforementioned different phenomena and to determine the nature and amount of the water absorption or plasticizer migration during aging.

A thermogravimetric instrument (TGT 92, Setaram, France), controlled by an Epson microcomputer (France), was used. The sample (a few milligrams) was introduced into a platinum crucible (the weighting was performed with a thermobalance under an inert argon atmosphere). The sample was heated from room temperature up to 450°C at a heating rate of 10°C/min.

Mechanical testing (which allowed the registration of the strain and stress at break) was performed on a universal tension machine (Adamel-Lhomargy, France) driven by a microcomputer (PC1600, Loga-Bax, France). Testing was performed on normalized samples (dog-bone shape;  $60 \times 60 \times 0.33$  mm<sup>3</sup>). The strain rate was equal to 50 mm/min.

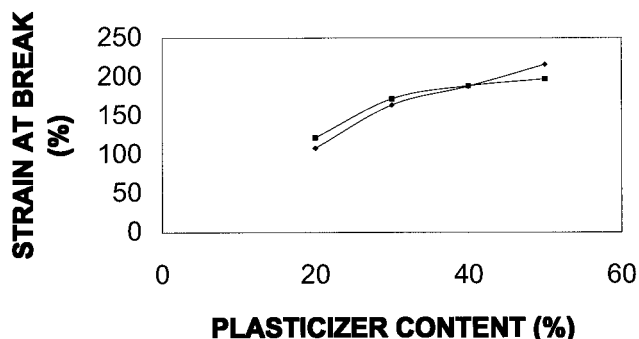
The dielectric measurements were carried out with a DEA 2970 dielectric analyzer (France), which allowed the measurement of the permittivity and dielectric loss over a wide range of frequencies (1 to 10<sup>6</sup> Hz) in the temperature interval from -100 to 150°C.

## RESULTS AND DISCUSSION

### Sample characterization of the different formulations before aging

#### Mechanical characterization

*Strain at break.* The mean values of the strain and stress at break were calculated with at least five sam-



**Figure 1** Evolution of the strain at break as a function of the plasticizer content: (◆) FxP and (■) FxA.

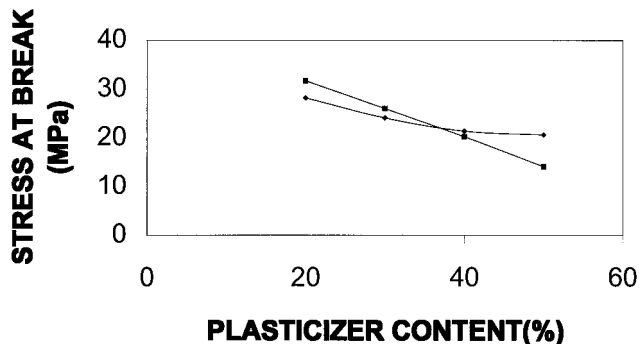


Figure 2 Evolution of the stress at break as a function of the plasticizer content: (◆) FxP and (■) FxA.

ples. Figure 1 shows an increase in the strain at break with a plasticizer content for both types of plasticizers. For a content lower than 40%, the strain at break of the DNA-plasticized samples was slightly higher than that of DOP-plasticized samples. At a 40% content, the strain-at-break values were the same for both types of samples. With more than 40% plasticizer, the inverse result was obtained: DOP-plasticized samples had a larger strain at break than the DNA ones. This mechanical behavior could be explained by the difference in the glass-transition temperatures and the viscosity difference of the two plasticizers: DNA presented a lower viscosity, and this enabled its insertion between

polymer chains, thereby reducing the interchain interactions.

*Stress at break.* The stress at break as a function of the plasticizer content for both types of samples is shown in Figure 2. This stress decreased sharply as the plasticizer content increased. This decrease was attributed to an increase in the elasticity (i.e., a decrease in the stiffness) of the samples. The same behavior encountered in the measurement of the strain at break was also observed in the measurement of the stress at break: at a 40% plasticizer content, the stress at break was the same for both types of samples. Above this content, DNA-plasticized samples had stress-at-break values lower than those of the DOP ones.

Determination of the onset decomposition temperature by thermogravimetry

Thermograms of different samples are shown in Figures 3 and 4. All of them have the same shape: the weight loss started around 250°C, accelerated when it reached 40%, and then slowed down around 350°C. This phase was attributed to the plasticizer loss and the evolution of chlorohydric acid, which resulted in polyene formation.<sup>4,6-9</sup> This loss was followed by a stability level attributed to polyacetylene, which is more stable than PVC.<sup>4</sup> Around 425°C, there was another weight loss, probably due to polyacetylene

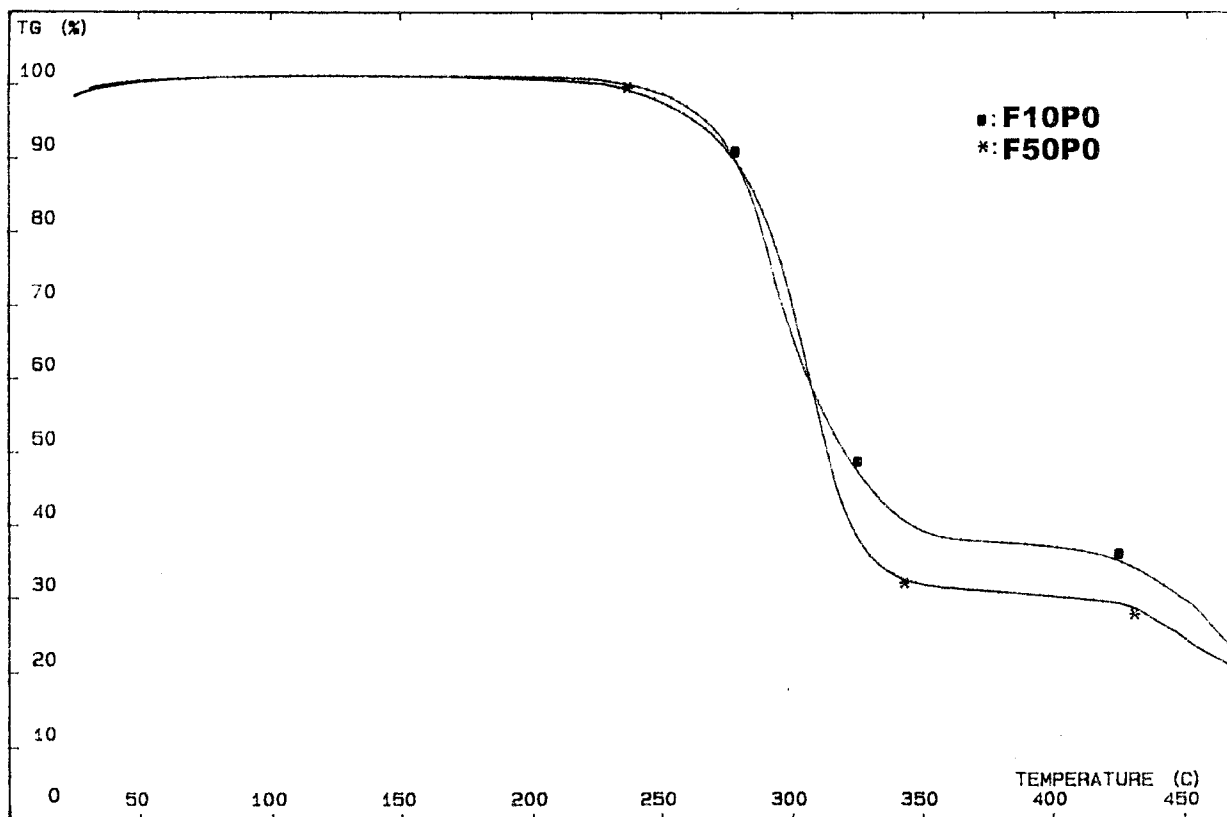


Figure 3 Thermograms of plasticized PVC samples with DOP at 10 and 50% contents.

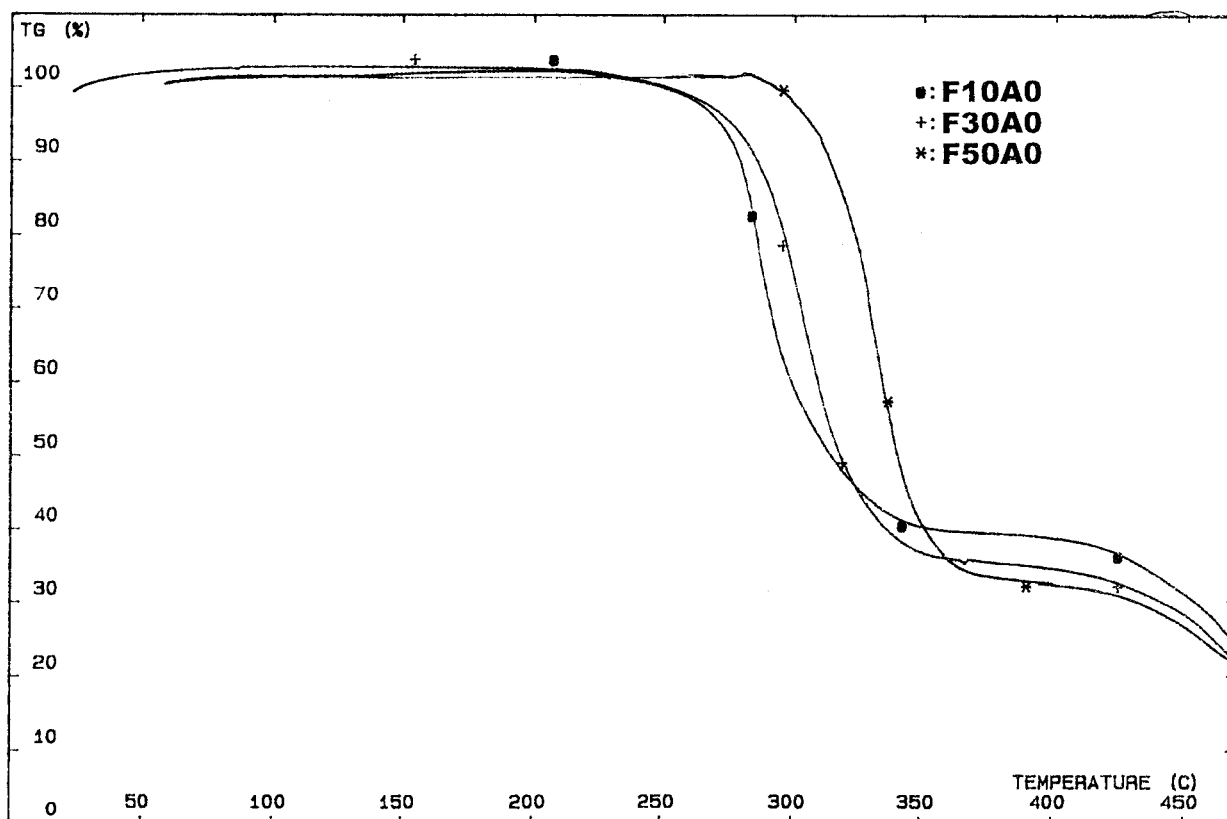


Figure 4 Thermograms of plasticized PVC samples with DNA at 10, 30, and 50% contents.

cracking. By an analysis of the thermograms of Figures 3 and 4, it can be postulated that the weight loss recorded in the 230–350°C temperature range was more important for the less plasticized samples. This phenomenon can be explained by the fact that the plasticizer delayed degradation; that is, the plasticizer had the advantage of ameliorating the stabilizer distribution and solvating the labile chlorine, thereby making the sample more stable.<sup>10–12</sup> The temperature at the beginning of the sample decomposition is shown in Table II; it was almost the same for all samples. Figures 5 and 6 present thermograms of 10% (DOP and DNA) and 50% (DOP and DNA) plasticized samples, respectively. In Figure 5, it can be observed that, for low plasticizer contents, both types of samples showed the same thermal behavior. However, for high plasticizer contents, as shown in Figure 6, better

thermal stability was obtained for the DNA-plasticized samples.

#### Sample characterization after water immersion

##### Weight variation

Figures 7–9 show the weight variation as a function of the immersion time for both DOP- and DNA-plasticized PVC samples. The curves present the same shape. The weight variation increased and then became constant before it decreased, reaching a negative value after 9 h of exposure for some formulations. Regardless of the nature of the plasticizer and its ratio, the weight variation was almost negligible ( $\leq 0.65\%$ ) within the experimental error.

According to a comparison of the color indices (according to the Synmero scale<sup>13</sup>) of the virgin and aged samples, there was no change, as expressed by the value of the color index being equal to unity. It can be concluded that during the hydrothermal treatment, there was no release of HCl vapors responsible for the formation of conjugated double bonds and discoloring.<sup>14</sup>

##### Determination of the plasticizer loss by thermogravimetry

So that the different phenomena occurring during hydrothermal aging could be distinguished, the subtraction

TABLE II  
Effect of Nature and Content of Plasticizer on the Temperature of the Decomposition Beginning

Temperature of the decomposition beginning for samples plasticized with DOP (°C)			Temperature of the decomposition beginning for samples plasticized with DNA (°C)		
F10P	F30P	F50P	F10A	F30A	F50A
235	235	235	235	235	287

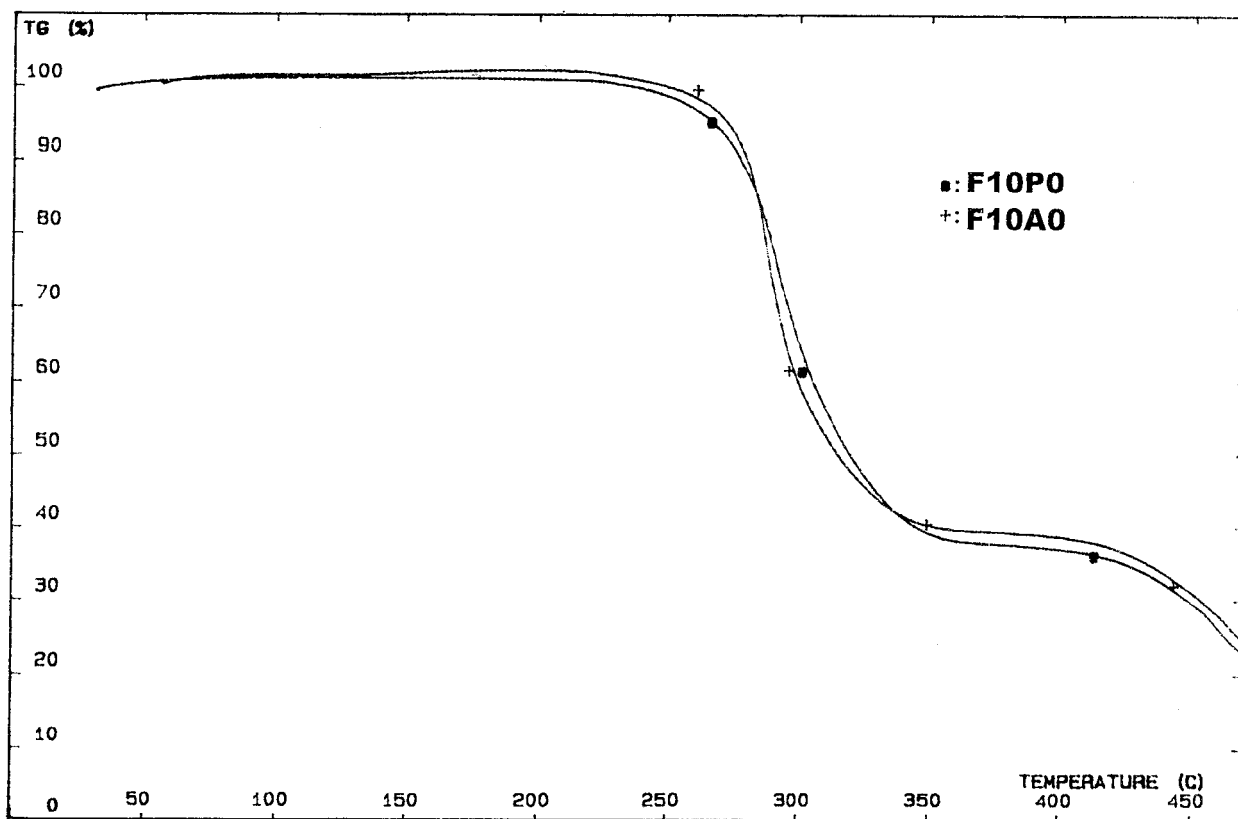


Figure 5 Thermograms of plasticized PVC samples with 10% DOP and 10% DNA.

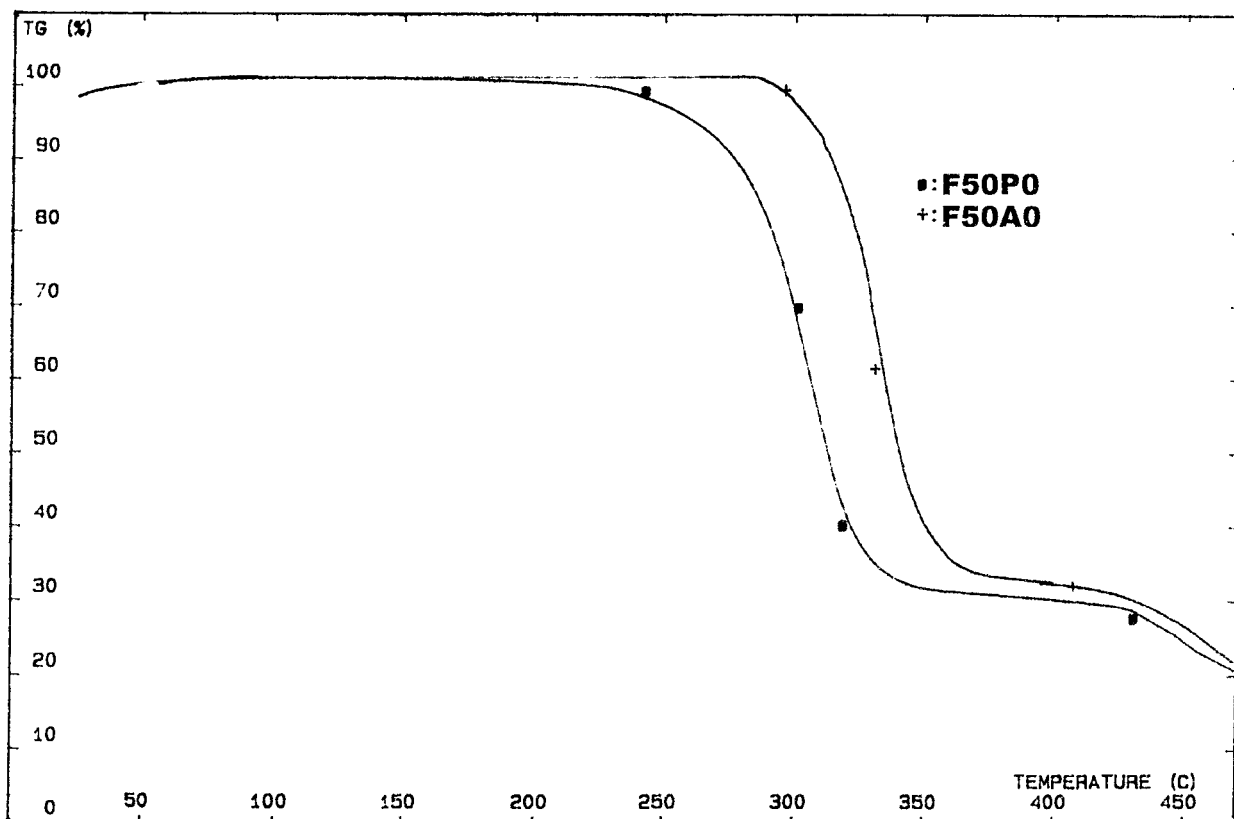
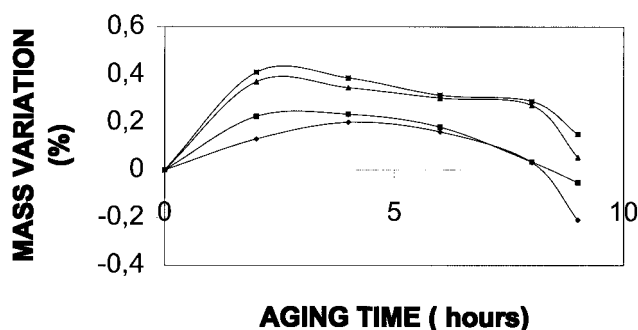


Figure 6 Thermograms of plasticized PVC samples with 50% DOP and 50% DNA.

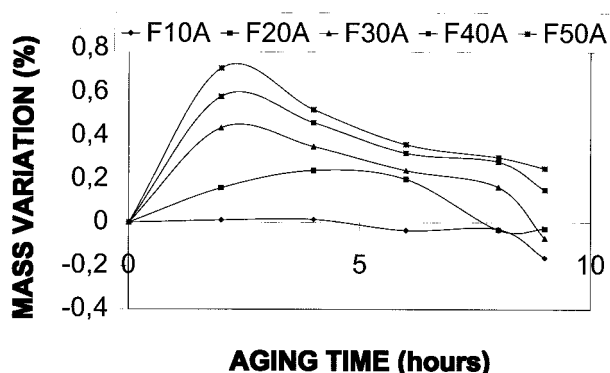


**Figure 7** Weight variation as a function of the immersion time in water at 100°C for plasticized PVC samples at 20, 30, 40 and 50% DOP: (◆) F20P, (■) F30P, (▲) F40P, and (●) F50P

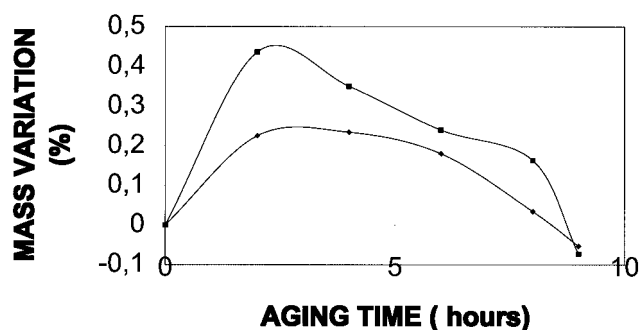
technique was used. This consisted of presenting, in the same figure, the thermograms of both virgin and aged samples. Between the first and second plateaus of stability, the total weight loss ( $w_t$ ) was attributed to the plasticizer weight ( $w_p$ ) and the weight of hydrochloric acid ( $w_a$ ). Because the amount of HCl was the same for all the samples, it could be established that, for a virgin material,  $w_{t(\text{virgin})} = w_{p(\text{virgin})} + w_{a(\text{virgin})}$  and that, for an aging material,  $w_{t(\text{immersed})} = w_{p(\text{immersed})} + w_{a(\text{immersed})}$  (where  $w_{t(\text{virgin})} - w_{t(\text{immersed})}$  is the weight loss of the plasticizer).

The applicability of this method for all the samples led to the results presented in Table III. Two examples of this treatment are shown in Figures 10 and 11.

A comparison of the thermograms shown in Figures 10 and 11 and the data summarized in Table III show that for the DOP-plasticized samples, and for the different contents used, the plasticizer did not migrate when it was in contact with water at 100°C, and the thermal stability was not affected. On the contrary, for the DNA-plasticized samples, the results revealed a migration of the plasticizer and a decrease in the thermal stability; as illustrated in Figure 11, the starting temperature of the decompo-



**Figure 8** Weight variation as a function of the immersion time in water at 100°C for plasticized PVC samples at 10, 20, 30, 40 and 50% DNA: (◆) F10A, (■) F20A, (▲) F30A, (●) F40A, and (▼) F50A.



**Figure 9** Weight variation as a function of the immersion time in water at 100°C for plasticized PVC samples at 30% DOP and 30% DNA: (◆) F30P and (■) F30A.

sition decreased from 275°C for F50A0 to 225°C for F50A9.

#### Mechanical characterization

**Strain at break.** Table IV clearly shows that, regardless of the nature of the plasticizer and its content, the samples underwent a reduction in the strain at break with the aging time (the period of immersion in water at 100°C). This decrease was sharper for the less plasticized samples. This can be explained by the fact that a small quantity of the plasticizer migrated rapidly, leaving microvoids in the PVC matrix that were filled with water. These results agree with those obtained for the weight variation test.

**Stress at break.** Table V shows that the stress at break decreased which the aging time. In principle, the plasticizer loss will induce a higher stiffness. However, in our case, the opposite happened, probably because the plasticizer migration was compensated by the water absorption.

#### Effect of the temperature, immersion time, nature, and concentration of the plasticizer on the dielectric properties

Figures 12–16 show that the profiles of the curves describing the variation of the permittivity as a function of temperature were similar for all the un plasti-

**TABLE III**  
Plasticizer Loss (wt%) of Samples Immersed in Water at 100°C for 10 h (as Measured by Thermogravimetric Analysis)

Sample	Loss of plasticizer (wt%) after water immersion at 100°C for a period of 10 h
F10P	0.0
F30P	0.5
F50P	0.5
F10A	5.0
F30A	4.0
F50A	2.5

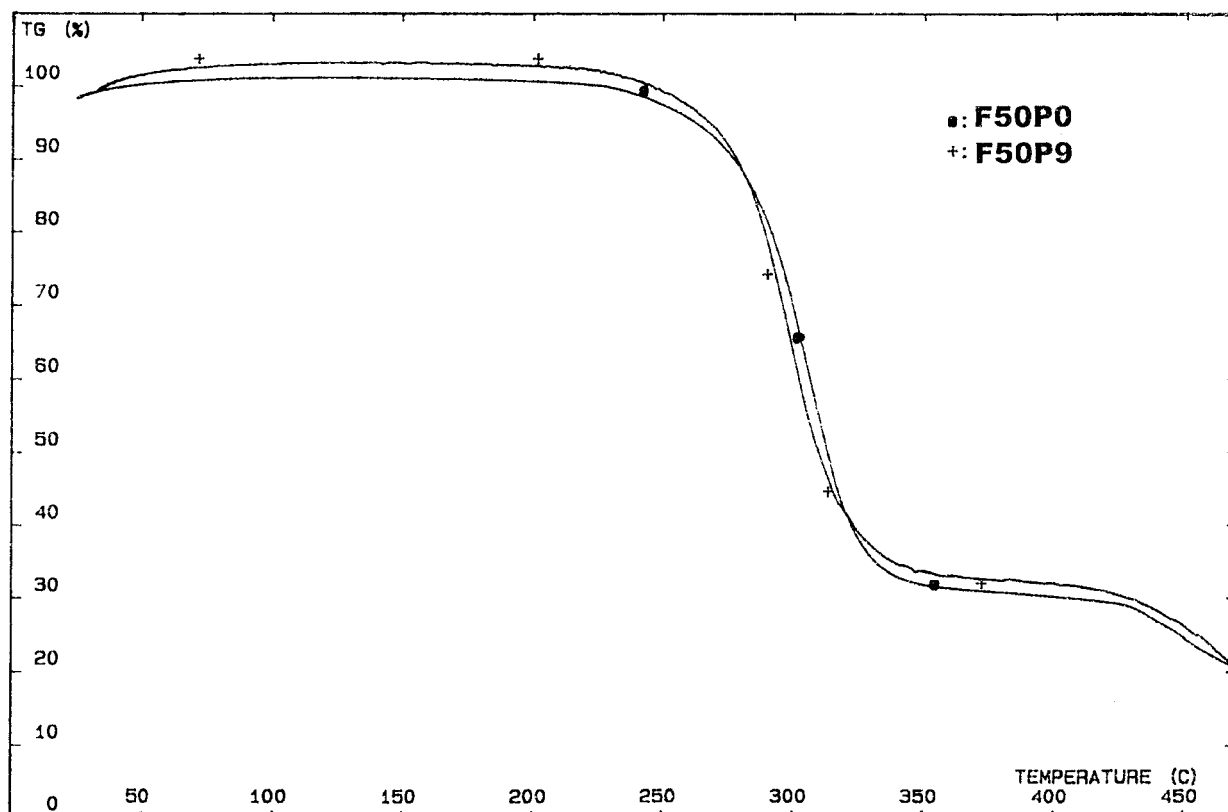


Figure 10 Thermograms of plasticized PVC samples with 50% DOP, virgin and immersed in water at 100°C (9 h).

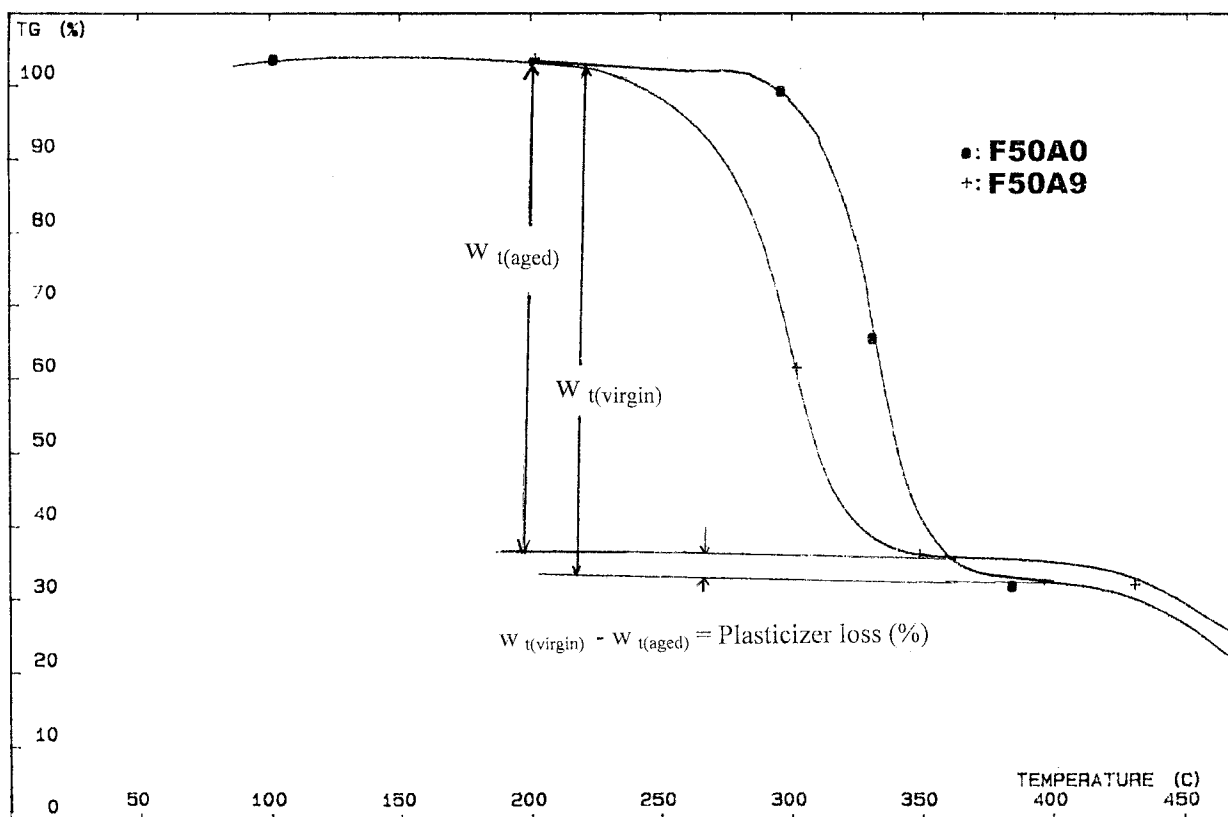


Figure 11 Thermograms of plasticized PVC samples with 50% DNA, virgin and immersed in water at 100°C (9 h).

**TABLE IV**  
**Effect of Hydrolytic Aging Time and the Nature, and Content of Plasticizer on the Strain at Break**

Formulation aging time (h)	Strain at break (%) of the samples plasticized with DOP				Strain at break (%) of the samples plasticized with DNA			
	F20P	F30P	F40P	F50P	F20A	F30A	F40A	F50A
0	109	164	188	216	122	172	189	198
2	52	151	183	212	108	166	182	193
6	54	141	181	204	111	139	178	189
9	96	143	180	211	119	136	164	182

cized and plasticized PVC samples, being independent of the frequencies and aging times.

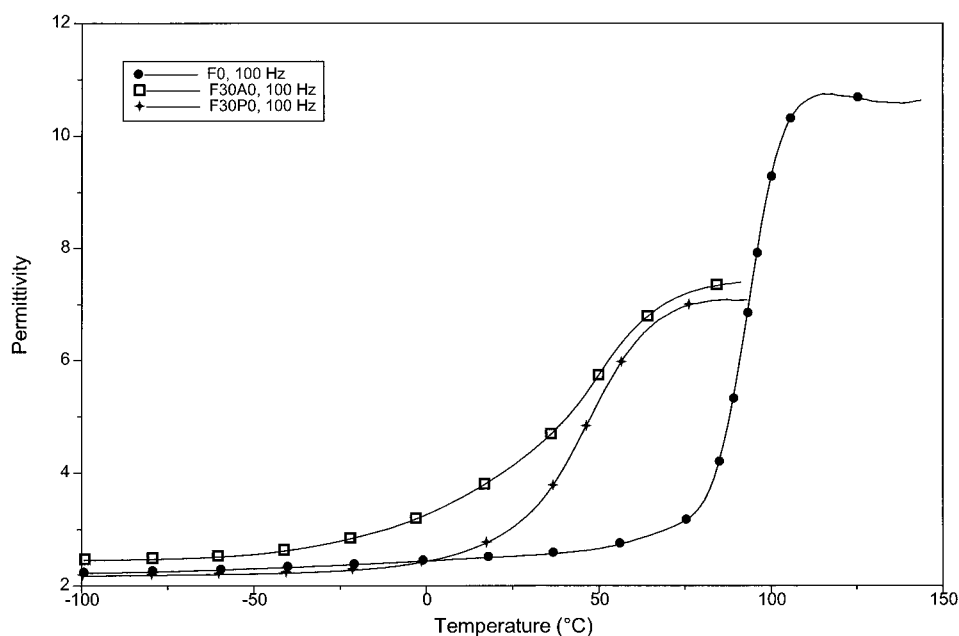
The dielectric permittivity had a constant value of 2.3 at  $-100^{\circ}\text{C}$  for all the samples. The general profile can be described as follows: a plateau starting from  $-100^{\circ}\text{C}$  and going up to almost  $+62$ ,  $-47$ , and  $-57^{\circ}\text{C}$  for unplasticized PVC, plasticized samples with DOP, and plasticized samples with DNA, respectively. This plateau was followed by a fast increase in the permittivity, and another was observed successively up to

$100^{\circ}\text{C}$  for unplasticized PVC and at  $+55^{\circ}\text{C}$  for both DOP- and DNA-plasticized samples.

In any case, the increase in the permittivity was dependent on the material polarity. In fact, the dipoles resulted from the formation of an electronic field along the asymmetric PVC chains, and in the absence of an electrical field, the dipoles were arbitrarily oriented; subsequently, the macroscopic polarization was inhibited. Under the electrical field, polarization changes were observed in the dielectric

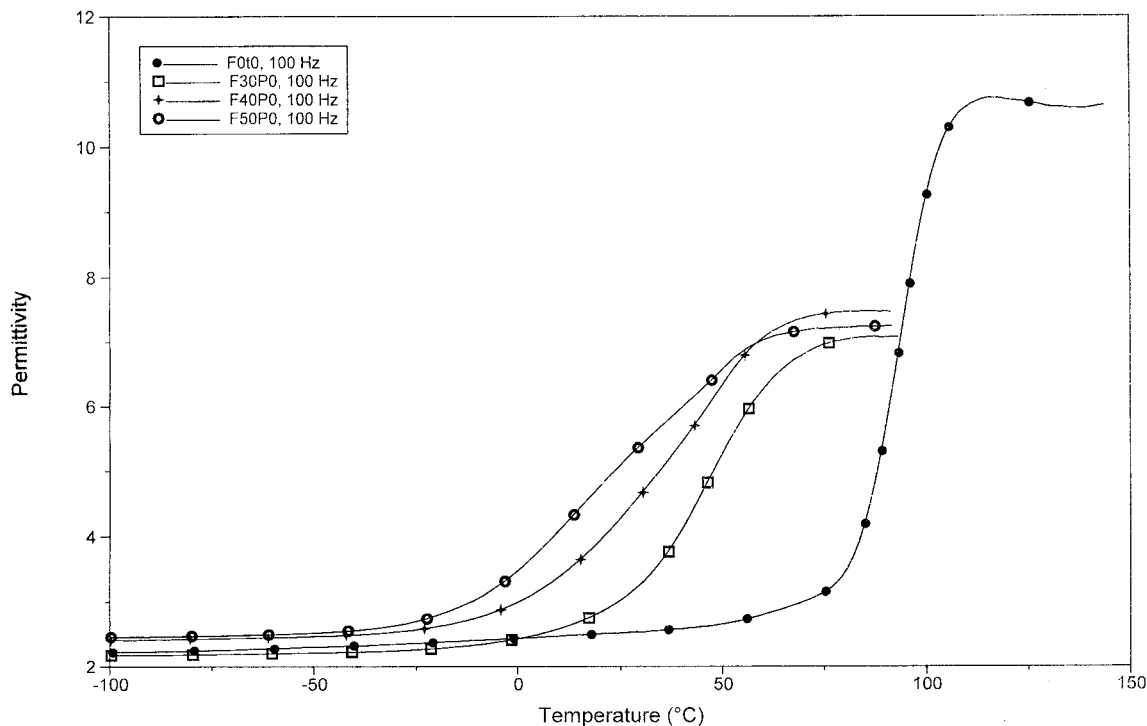
**TABLE V**  
**Effect of Hydrolytic Aging Time and the Nature and Content of Plasticizer on the Stress at Break**

Formulation aging time (h)	Stress at break (MPa) of the samples plasticized with DOP				Stress at break (MPa) of the samples plasticized with DNA			
	F20P	F30P	F40P	F50P	F20A	F30A	F40A	F50A
0	28.2	24.11	21.40	20.65	31.73	26.05	20.26	14.10
2	25.7	21.60	19.90	18.45	28.70	25.95	19.30	13.90
6	24.3	19.50	18.40	16.70	29.73	27.90	22.73	13.80
9	25.8	20.80	20.30	17.40	30.83	25.83	22.30	15.63



**Figure 12** Evolution of the permittivity at 100 Hz as a function of temperature for unplasticized and plasticized PVC samples with 30% DOP and 30% DNA.

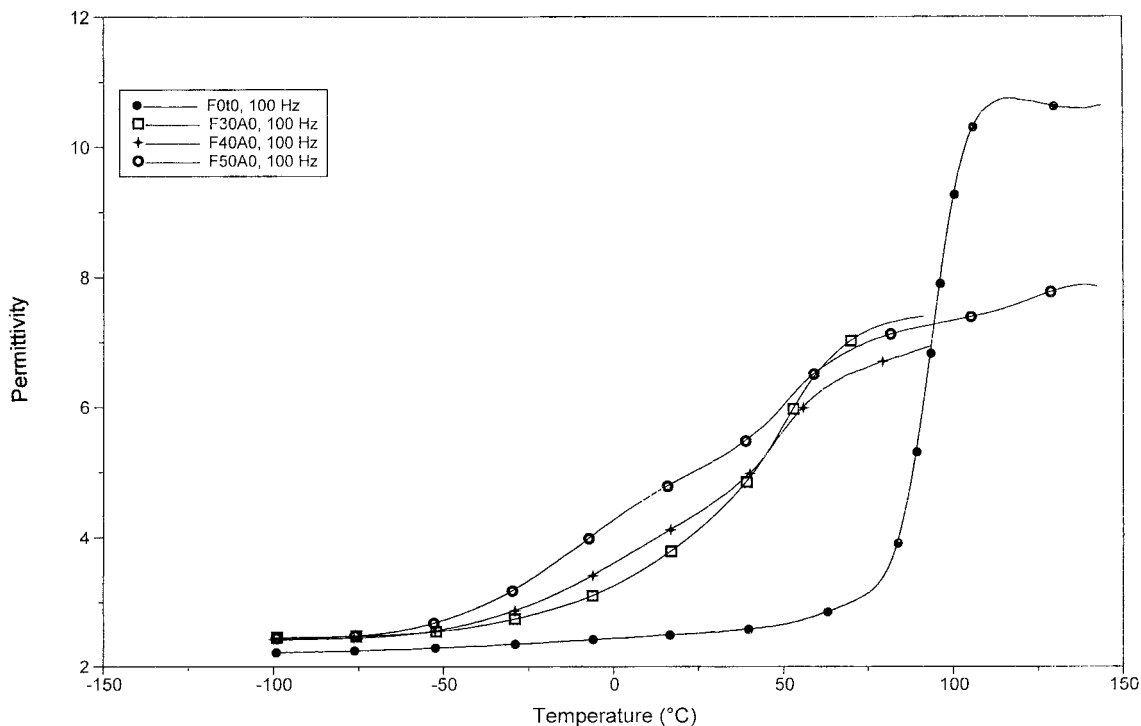




**Figure 13** Evolution of the permittivity at 100 Hz as a function of temperature for unplasticized and plasticized PVC samples at 30, 40, and 50% DOP.

materials. These dipoles were subjected, according to Coulomb's law, to a couple of forces that tended to orient them. However, these forces could be con-

strained by thermal agitation. This increase in the permittivity with temperature can also be explained by both the mobility of the polar groups and the



**Figure 14** Evolution of the permittivity at 100 Hz as a function of temperature for unplasticized and plasticized PVC samples at 30, 40, and 50% DNA.

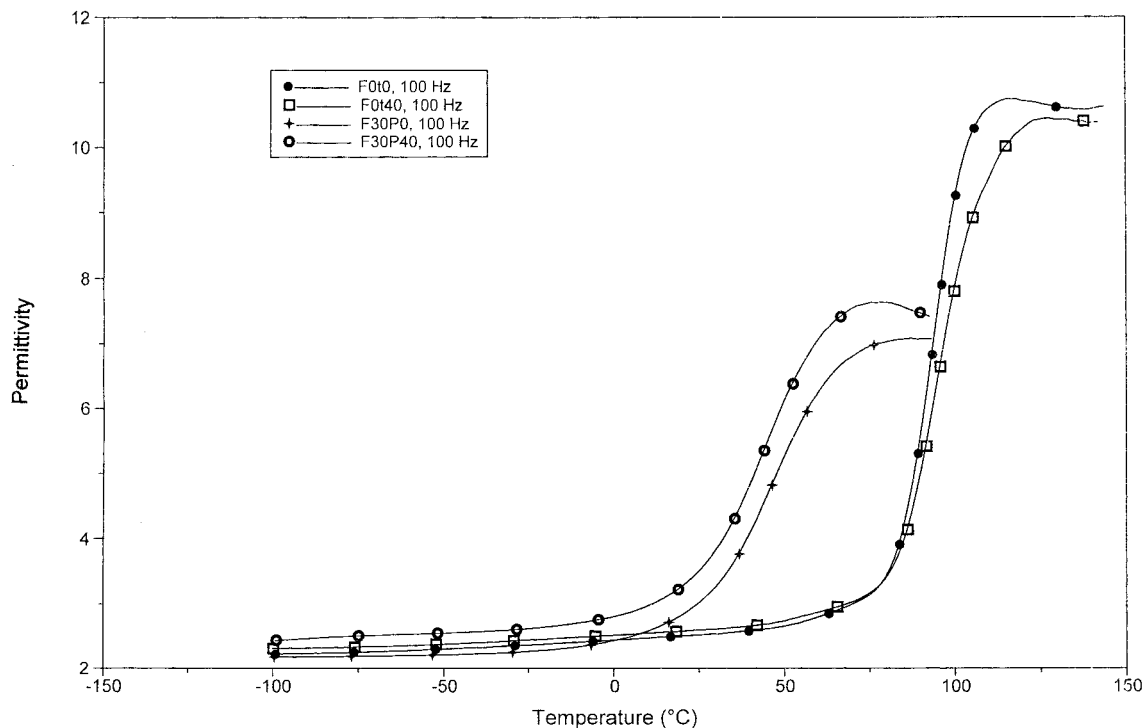


Figure 15 Effect of the water immersion on the permittivity at 100 Hz of unplasticized and plasticized samples at 30% DOP.

reduction in the density, which favored the orientation of the groups.<sup>15-17</sup>

Table VI shows that the temperature corresponding to the beginning of the fast increase in the permittivity

was lower for the plasticized samples than for the unplasticized samples; it became lower as a sample was more plasticized. However, it was lower for samples plasticized with DNA. This could be attributed to

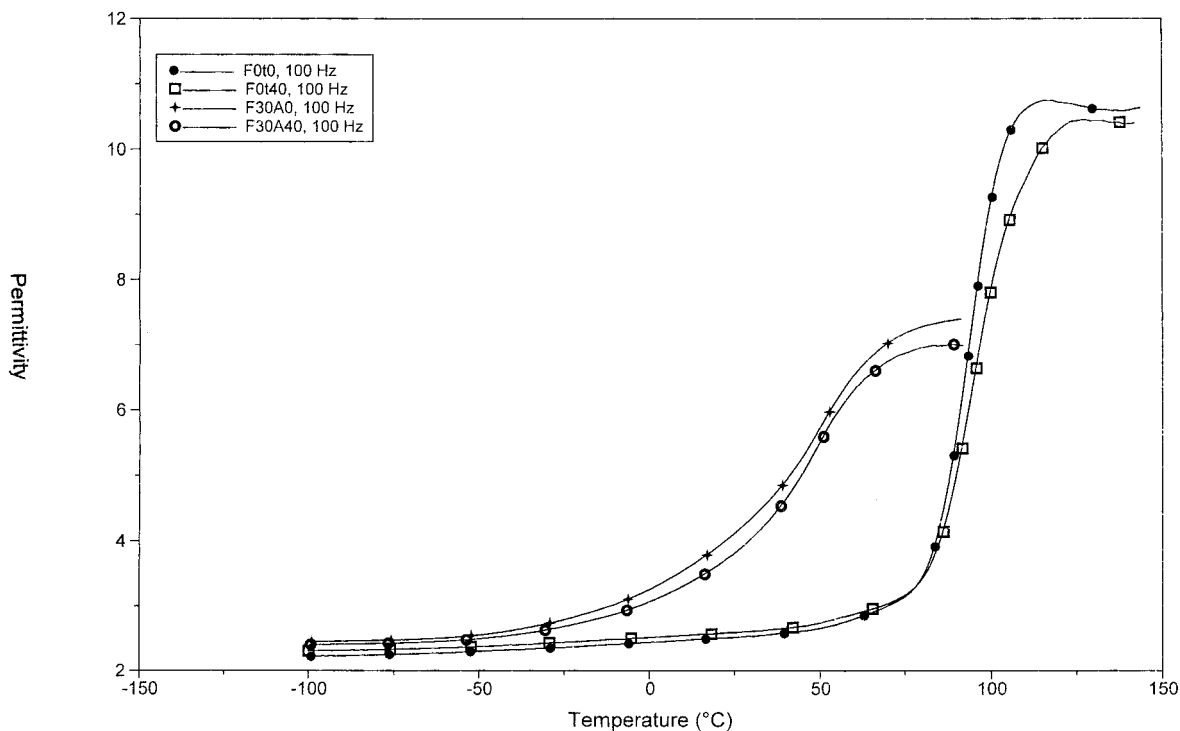


Figure 16 Effect of the water immersion on the permittivity at 100 Hz of unplasticized and plasticized samples at 30% DNA.

**TABLE VI**  
**Temperature Corresponding to the beginning of the Fast Increase in the Permittivity**

	Plasticizer content (% <sup>1</sup> , w/w)		
	30	40	50
Temperature corresponding to starting of the fast increase in the permittivity (°C)			
DOP	12	-14.7	-26.1
DNA	-28.5	-38.5	-51.2
Pure PVC	69.2		

the plasticization rate, which allowed the mobility of the macromolecular chains. Moreover, the decrease in density was due to the fact that for the same plasticization rate, DNA reduced the cohesion forces between the chains more than DOP did.

Figure 15 shows that the plasticized PVC samples with DOP and subjected to aging had an increase in their permittivity. The latter was attributed to the absorption of a small amount of water. In contrast, Figure 16 shows that the permittivity of the plasticized PVC samples with DNA and subjected to aging decreased slightly. This could be attributed to the loss of the plasticizer during exposure, which tended to reduce the polarity of the material.

For the unplasticized samples, a slight difference in the permittivity was noted at low temperatures (the first plateau of stability); in the area corresponding to the increase in the permittivity, a difference was observed too. This means that the permittivity of the aged sample was lower than that of the unexposed one. This result could easily be attributed to the decrease in the number of chlorine atoms in the aged samples (reduction in the electrical dipoles) due to deshydrochlorination.

## CONCLUSIONS

From this study, the following conclusions can be drawn.

The thermogravimetric method for testing the thermal stability of plasticized PVC is among the techniques that can be used to separate the different phenomena occurring during aging and to determine the quantity of plasticizer migration with high precision.

Under hydrothermal conditions, formulations based on DNA are limited because of the migration phenomenon of the plasticizer in water. However, the use of DOP is recommended for drying at medium and higher temperatures.

Mainly for electrical applications, in cable coverings, less plasticized samples are more useful because of their lower permittivity, and DOP is recommended because the temperature corresponding to the fast increase in its permittivity is relatively higher.

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