Thermal Aging of Plasticized PVC. II. Effect of Plasticizer Loss on Electrical and Mechanical Properties

L. AUDOUIN,[1,*] B. DALLE,[2] G. METZGER,[2] and J. VERDU[1]

[1]ENSAM, 151 Bd de l'Hôpital, 75013 Paris, France; [2]EDF/DDR, 1 av. du Général De Gaulle, 92141 Clamart Cedex, France

SYNOPSIS

The change of mechanical properties was followed during thermal aging at 85, 95, 105, and 120°C of the 10 PVC–didecylphthalate extrudates studied in the first part of this paper, but also of four new samples differing only by the plasticizer concentration. For these latter samples, the change of dielectric properties was also studied. It appears that the dielectric properties are essentially the function of the plasticizer concentration whatever is the initial concentration or aging conditions. In contrast, the mechanical properties vary in a more complex way and cannot be predicted by a simple physical model. It is suggested that, among other factors, the depth distribution of plasticizer can play an important role.

INTRODUCTION

The effects of plasticizer concentration on mechanical[1-4] or dielectric[5-10] properties of PVC were widely studied in the past decades.[11] The main effect of concentration changes is obviously the shift of the glass transition temperature, T_g, for which many theoretical models are available, including very recent developments.[12]

All these theories allow us to define a critical mass fraction, m_g, or a volume fraction, v_g, for which the glass transition occurs at ambient temperature. In the simplest approach,[13] the critical value of volume fraction would be nearly constant: $v_g = 0.22$–0.30.

In the case of plasticizer loss by evaporation, this critical point would be reached when the loss weight fraction would be w_g, such as:

$$w_g = m_p \left[\frac{m_a}{m_p} - \frac{v_g}{1 - v_g} \cdot \frac{\rho_a}{\rho_p} \right] \qquad (1)$$

where m is a mass fraction in the virgin sample and ρ is the density (a and p designate, respectively, the plasticizer and the polymer). In industrial extrudates for electrical insulation, the orders of magni-

tude are typically $\rho_a/\rho_p \simeq 0.70$, $m_a \simeq 0.25$, and $m_p \simeq 0.5$, which leads to critical weight losses of 10% (for $v_g = 0.30$) to 15% (for $v_g = 0.22$).

Indeed, for mechanical or electrical properties determined at ambient temperature, very strong changes are to be expected when the loss weight fraction w approaches w_g, and the initially rubbery material becomes progressively a glass.

From a mechanical viewpoint, the main effects of a decrease of the plasticizer concentration are the increase of the ductile–fragile transition temperature and the increase of stiffness.[2] In the tensile tests, nonmonotonic variations of the ultimate or yield stresses can be observed as a result of antiplastification effects.[14,15] In contrast, the ultimate elongation ϵ_R decreases monotonically. Various authors have studied the consequences of plasticizer loss on mechanical properties,[16-19] but the problems of time-life prediction were not examined.

The effects of thermal aging on dielectric properties were reviewed by Hedvig.[9] The loss peak corresponding to the transition increases in intensity and is shifted toward high temperatures. The same author devoted a chapter of his book to the changes of AC conductivity due to the formation of conductive species during thermochemical processes (HCl, chlorides, etc).

As was shown in the first part of this article,[20] models of relatively good predictive value can be en-

visaged for the weight-loss kinetics. On the other hand, physical studies on virgin samples allow the establishment of the relationship between physical properties and plasticizer concentration (for a given plasticizer). Is it then possible to predict the change of physical properties from the weight-loss data during thermal aging? In other words, is an aged sample equivalent to a virgin sample having the same plasticizer concentration? The aim of the present part of this article is to try to answer these questions in the case of tensile ultimate properties and dielectric dissipation factor tan δ measured at ambient temperature for the PVC–didecylphthalate (DDP) system.

EXPERIMENTAL

Materials

Two series of samples were studied. The first one (I) corresponds to samples A–H described in the first part of this paper.[20] The second one (II) is based on four PVC recipes described in Table I, in which DDP concentration was, respectively, 15, 20, 25, and 30%, all the other composition parameters being constant. The samples of series II were also extruded ribbons of 1.5 ± 0.2 mm thickness.

Aging

The thermal aging tests were performed in ventilated ovens regulated at 85, 95, 105, and $120 \pm 1°C$. The samples were deposited on inox grids to avoid creep deformation under their proper weight. The series I and II differ essentially by the sample mass/oven volume ratio, which was about $2.5 \cdot 10^{-3}$ g/cm^3 in series I and 10^{-3} g/cm^3 in series II.

Testing

Weight losses were determined as described in the first part of this paper for all samples under study.[20]

Tensile properties were measured at 21°C using an ISA machine equipped with an extensometer.

Table I Composition of Samples of Series II

Sample	Plasticizer (%)	ν_0 Plasticizer/PVC	Thickness (mm)
15	15.10	0.22	1.4
20	20.04	0.31	1.5
25	24.89	0.41	1.3
30	29.60	0.52	1.4

The tensile rate was 50 mm/min for a calibrated length of 25 mm on dogbone samples according to the French Standard NFT 510340. The reported values are averaged over five measurements on samples taken at random in the oven volume (in order to minimize the eventual effects of the temperature-field heterogeneities).

Dielectric properties were measured using a Digibridge 1689 instrument (Genard) at 21°C and, occasionally, at other temperatures. The measurements were made on circular samples of 10 mm diameter cut in the ribbons. A conductive foil 3M 1181 of $32 \cdot 10^{-3}\Omega$ cm^{-2} resistivity was placed at the sample surface, according to the French Standard NFC 26230. Measurements were made at various frequencies between 60 and 10^5 Hz. The discussion will be essentially focused on the values of tan δ determined at 0.5 and 50 kHz.

RESULTS

Mechanical Properties

Initial Data

As expected, the ultimate tensile properties are essentially governed by the plasticizer/PVC mass ratio ν_0, although other factors such as the filler content (which reduces the ultimate strain) and the macromolecular orientation (depending on processing conditions) are presumably involved and are possible sources of data scatter.

Anyhow, both series behave as theoretically expected: The ultimate strain ϵ_R is an increasing function of ν_0 and the ultimate stress σ_R is a decreasing function of ν_0, except perhaps for $\nu_0 < 0.3$, where antiplastification effects can occur (Fig. 1).

In the simplest case, the representative point of a given sample must remain on its curve and move toward the left during its thermal aging.

Thermal Aging of Series I

Examples of kinetic curves of ultimate strain changes during thermal aging are presented in Figure 2. As expected, ϵ_R decreases first slowly until a critical exposure time, after which it decreases more or less abruptly to reach very low values typical of the glassy state. Indeed, the critical exposure time is a decreasing function of the temperature: It is a few days at 120°C and more than 1 year at 85°C for the majority of the samples. The characteristic decrease of ultimate strain begins in practically all cases when the latter has a loss about $\frac{1}{4}$ of its initial
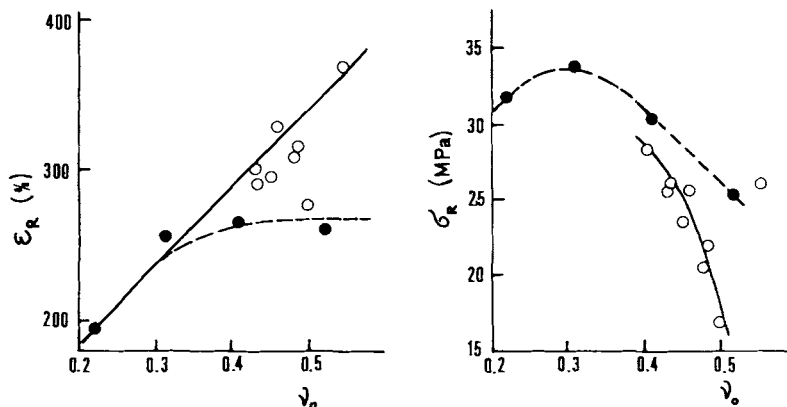
Figure 1   Ultimate strain (left) and ultimate stress (right) of samples under study against plasticizer/PVC mass fraction: (○) series I; (●) series II.

value, so that it appeared interesting to define a "mechanical lifetime" $t(75)$ as the exposure duration needed to reach an ϵ_R value equal to 75% of its initial value.

In Figure 3, correlation was attempted of the reciprocal of lifetime $[t(75)]^{-1}$ to the weight-loss rate r as determined in the preceding part of this article.[20] The following comments can be made concerning these results:

(i) There is generally a correlation between the "mechanical lifetime" and the weight-loss rate.

(ii) This correlation is not valid for sample C, whose lifetime is considerably shorter than expected. As quoted in the first part of this article,[20] this sample has an especially low thermochemical stability and becomes black during its aging. Solubility determinations revealed in this case an extensive cross-linking that is obviously the cause of the quick ultimate strain decrease. Incidentally, such plots $[t^{-1}, r]$ could allow separation of the effects of the PVC degradation and plasticizer loss during thermal aging.

(iii) The slope of the correlation straight line is not independent of the aging conditions; for instance, we can write

$$[t(75)]^{-1} = K \cdot r$$

K (dimensionless) = 0.10 at 105°C and 0.22 at 95°C.

In other words, the change of ϵ_R depends not only on the plasticizer weight loss, but also on the aging conditions. This is well illustrated in Figure 4, where ϵ_R was plotted against weight loss. Distinct exposure conditions correspond clearly to distinct curves; the

loss of ultimate strain for a given weight loss seems to be often a decreasing function of the exposure temperature, but there is no systematic trend.
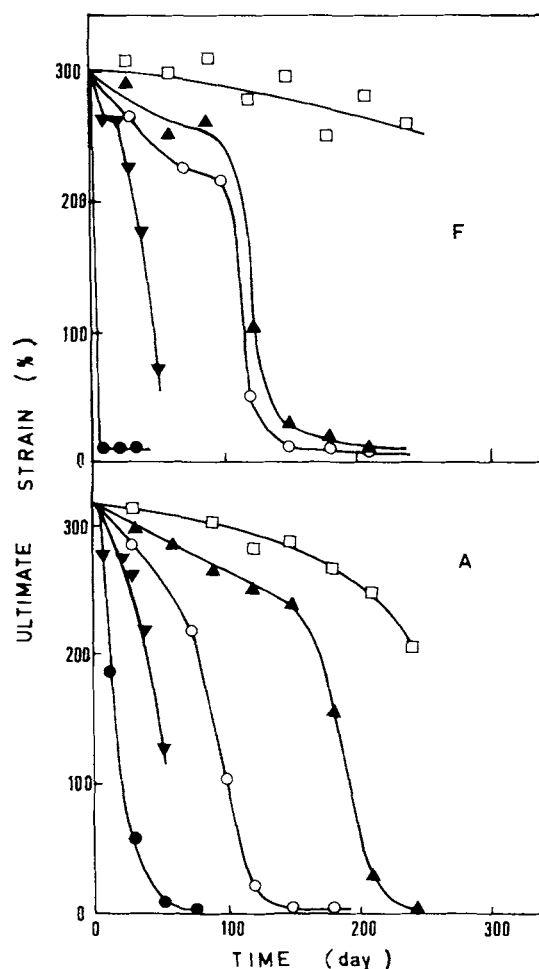
Figure 2   Examples of kinetic curves of ultimate strain changes for samples of series I: (a) **F**; (b) **A**; (□) 85°; (▲) 95°; (○) 105°; (▼) 110°; (●) 120°.
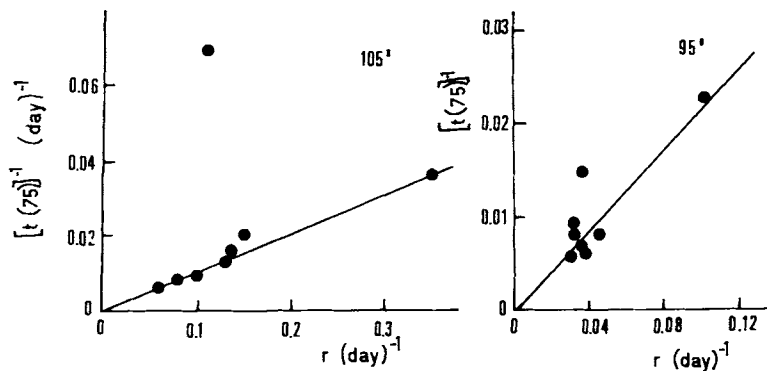
Figure 3   Reciprocal of the lifetime against plasticizer weight-loss rate for exposure temperature of 95°C (right) and 105°C (left) for samples of series I.

Thermal Aging of Series II

Some results obtained with series II are summarized in Figure 5, where the ultimate elongation was plotted against the residual plasticizer concentration. Here, the change of mechanical properties appears practically independent of exposure conditions. The ductile–brittle transition occurs in the 13–15% concentration range for all the samples except the 25% one, for which it is located between 15 and 20%, which is presumably due to a change in extrusion conditions. The behavior of the samples displays, however, some unexpected features, especially a small but significant decrease of ϵ_R in the initial aging period, after which it reaches to a plateau value of 225–240% independent of the initial plasticizer concentration.

In Figure 6, the ultimate stresses were plotted against ultimate strains for all the samples and exposure conditions under study. The figure reveals the complexity of the aging behavior of plasticized PVC. As a matter of fact, in the simplest case where the ultimate properties would depend only on the residual plasticizer concentration, all the points would be located on an unique rupture envelope, which is not the case for the experimental data.

Dielectric Properties of Series II

Examples of dielectric spectra (at ambient temperature) of virgin and aged samples are presented in Figure 7. Tan δ measured at, respectively, $5 \cdot 10^2$ and $5 \cdot 10^4$ Hz was plotted in Figure 8 against the residual plasticizer concentration. Here, the change of tan δ appears practically independent of the exposure conditions or initial plasticizer concentration. For instance, in the 13–30% concentration range, it could be written as
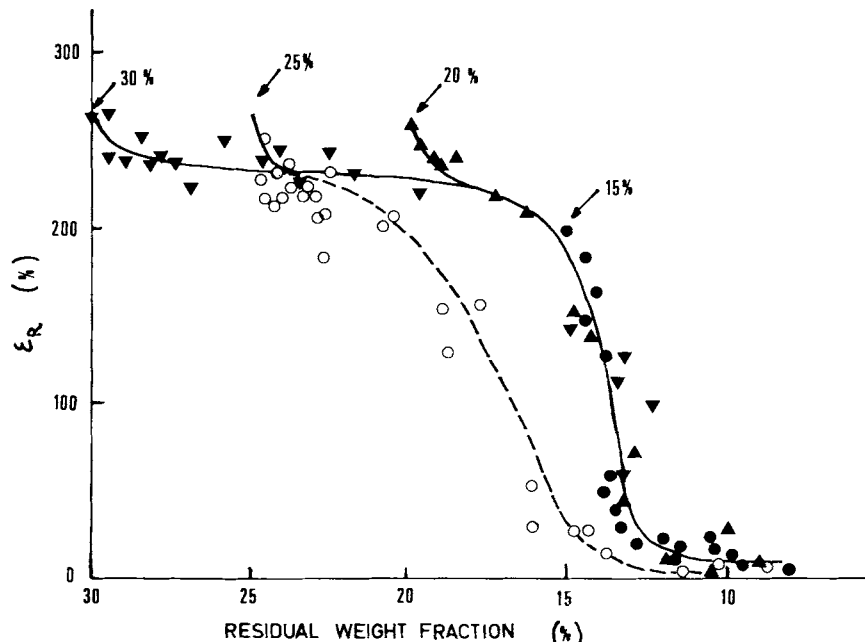
$$\tan \delta (50 \text{ kHz}) = 3.7 \cdot 10^{-3}(p - 9.5)$$

where p is the residual plasticizer concentration expressed in weight percent.

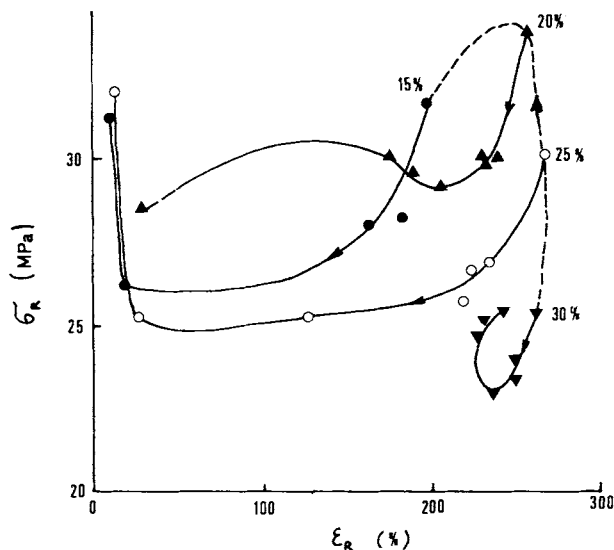Indeed, the monotonic character of the $(\tan \delta - p)$
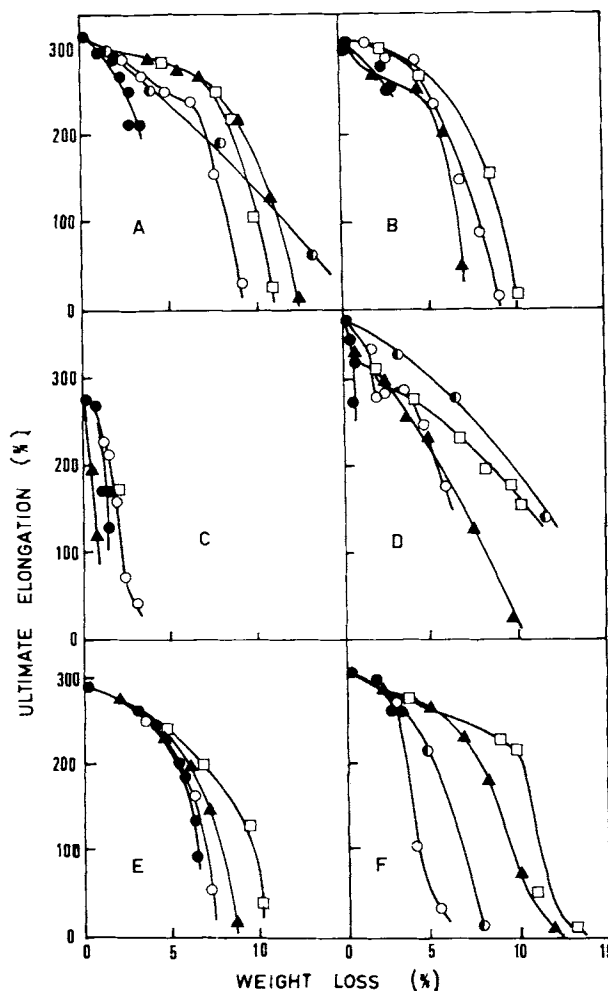
Figure 4   Examples of curves of ultimate strain against weight loss for samples of series I: (●) 85°; (○) 95°; (□) 105°; (▲) 110°; (◐) 120°.

Figure 5   Ultimate elongation against residual weight fraction of plasticizer for samples of series II.

curve is due to the choice of the temperature of dielectric measurements, as schematized in Figure 9, where the dissipation bands corresponding to three aging stages are presented.

The temperature T_1 corresponds to the chosen experimental conditions: T_1 is close to the glass transition temperature (at the frequency under consideration) of the most plasticized sample (30%). Since the plasticizer loss results in a shift of the dissipation band toward high temperatures, tan δ must monotonically decrease.

A monotonic decrease would be also observed for $T_2 \ll T_1$, but its amplitude would be considerably lower.

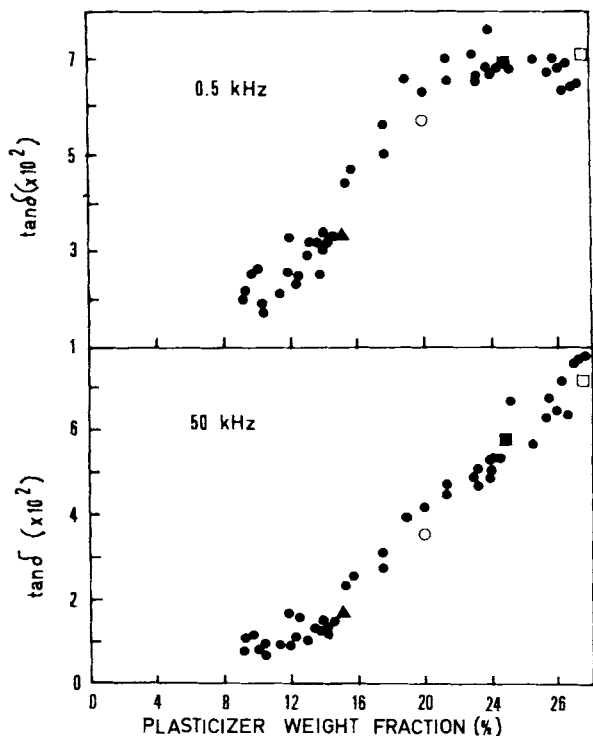**Figure 6**   Rupture envelopes for samples of the series II.
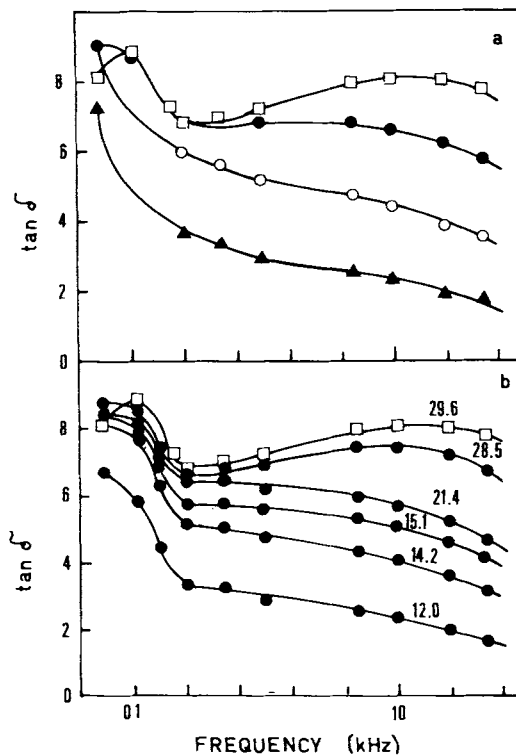
Figure 7   Examples of dielectric spectra taken at 21°C (a) for virgin samples (□) 30%, (●) 25%, (○) 20%, (▲) 15%, and (b) aged samples of 30% of series II.

For symmetric reasons, a monotonic increase is expected at T_3 close to the glass transition temperature of unplasticized PVC. In contrast, nonmonotonic variations are to be expected at any temperature included between the glass transition temperatures of the most plasticized sample and unplasticized PVC (Fig. 9).
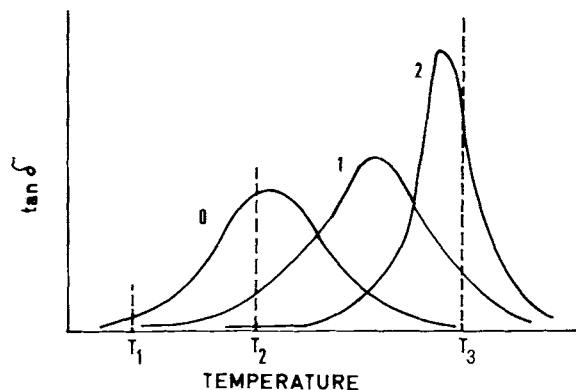
DISCUSSION

From the above results, it can be concluded that the dielectric property changes can be reasonably predicted from the overall weight-loss data, provided that tan δ is measured just below the initial glass transition temperature. In the case of industrial samples of PVC plasticized by less than 30% by weight of DDP, measurements at ambient temperature, a 25–50 kHz frequency would be convenient.

More complicated is the problem of ultimate mechanical properties. The results of the kinetic study of weight loss suggest a possible explanation for observed behavior. It was shown in the first part of this article that there are two kinetic regimes controlled, respectively, by the plasticizer diffusion and evaporation. The corresponding thickness profiles
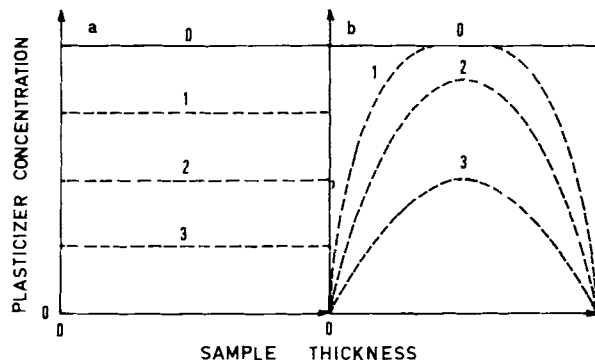
Figure 9 Schematization of the shift of the dissipation band: (0) unaged sample; (1) aged sample; (2) completely deplasticized sample. For significations of T_1, T_2, $\cdots$ (see text).

of plasticizer concentration are schematized in Figure 10. Indeed, the failure of an heterogeneous sample having a soft core between two stiffer superficial layers is not necessarily the same as for a homogeneous sample having the same average stiffness. It could be, for instance, supposed that the rupture is essentially controlled by the crack initiation in the superficial layer, the latter being easier as the local plasticizer concentration decreases. The role of this superficial deplasticization can explain the fact that the ductile–brittle transition occurs often in the range 20–15% (overall residual plasticizer concentration) for the series I samples, whereas calculations predict, rather, a value of 10–15%, as shown in the Introduction.

The heterogeneity of the depth distribution of the plasticizer after thermal aging was experimentally confirmed for one sample (initial plasticizer concentration 20%) by ester FTIR titration on the microtome sections (Fig. 11). In the case under con-

Figure 8 Tan δ against residual plasticizer concentration for all samples of the series II; measurements made at 21°C and 0.5 Hz (a) and 50 kHz (b): ($\square$) virgin sample of 30%, ($\blacksquare$) 25%, ($\bigcirc$) 20%, and ($\blacktriangle$) 15%.

Figure 10 Schematization of thickness profiles of plasticizer concentration in the case of diffusion (right) and evaporation (left) kinetic control: (1,2,3) successive steps of ageing; (0) the unaged sample.
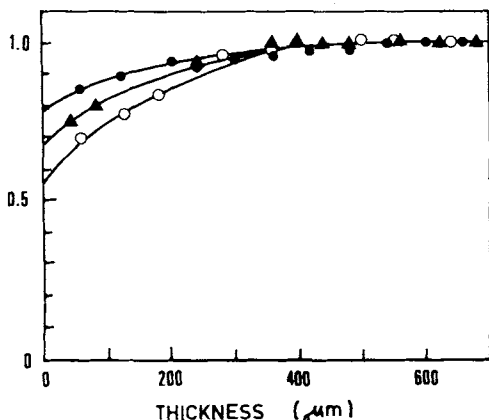
Figure 11 Experimental (normalized) thickness profile for samples 20%, in which the residual plasticizer concentration is 15%: (●) 120; (▲) 105, (○) 95°C.

sideration, the concentration gradient appears as a decreasing function of the temperature. In other words, for a given overall residual plasticizer concentration of 15%, the sample aged at 95°C appears more heterogeneous than those aged at 105 or 120°C, which is consistent with the data of Figures 3 and 4.

Differences in plasticizer distribution within the thickness cannot, however, explain all the features of the changes of ultimate properties, especially the unexpected decrease of ϵ_R in the early period of exposure, which is well put in evidence in Figure 5. Physical changes due to orientation relaxation and other annealing effects are probably involved in this phenomenon, which seems to be difficult to attribute to plasticizer loss.

In conclusion, the dielectric properties and, presumably the viscoelastic properties, can be considered as the average values of the contribution of elementary layers distributed into the sample thickness. For this reason, they are only a function of the residual plasticizer content when, indeed, the thermochemical degradation of PVC can be neglected. For these properties, the kinetic model for the lifetime prediction can be envisaged on the basis of the weight-loss kinetic analysis made in the first part of this article.[20]

Concerning ultimate mechanical properties, however, supplementary investigations on the fail-

ure characteristics of heterogeneous samples will be needed.

At the same time, methods of prediction of the depth profile of the plasticizer concentration are to be developed. They need considerable refinement of the kinetic study of weight loss.

REFERENCES

1. S. L. Brous and W. L. Semon, *Ind. Eng. Chem.*, **27**, 667 (1935).
2. R. F. Clash and R. M. Berg, *Mod. Plast.*, **21**(11), 119–124, 160 (1944).
3. R. F. Boyer and R. S. Spencer, *J. Polym. Sci.*, **2**, 157 (1947).
4. R. F. Taylor and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **8**, 1563 (1964).
5. R. M. Fuoss and J. O. Kirkwood, *J. Am. Chem. Soc.*, **63**, 385 (1941).
6. L. Nielsen et al., *J. Appl. Phys.*, **21**, 607 (1950).
7. G. Pezzin and A. Paglian, *Chem. Ind. (Milan)*, **48**, 458 (1966).
8. P. Hedvig, *J. Polym. Sci. A*, **7**, 1145 (1969).
9. P. Hedvig, *Dielectric Spectroscopy of Polymers*, Adam Hilger, Bristol, 1977.
10. G. P. Mikhailov, A. I. Artychov, and T. I. Borisova, *Vysokomol. Soed. B*, **9**, 138 (1967).
11. Review in S. K. Sears and J. R. Darby, *The Technology of Plasticizers*, Wiley, New York, 1982.
12. A. Di Benedetto, *J. Polym. Sci. B*, **25**, 1949 (1988).
13. A. M. Berens, *J. Appl. Polym. Sci.*, **27**, 9014 (1989).
14. L. Bohn, *Kunststoffe*, **53**, 826 (1963).
15. G. Pezzin, G. Ajiroldi, and C. Garbuglio, *J. Appl. Polym. Sci.*, **11**, 255 (1967).
16. E. M. Smoley, *J. Appl. Polym. Sci.*, **20**, 217 (1976).
17. J. Sparks and D. W. Young, *Ind. Eng. Chem.*, **41**, 665 (1949).
18. P. Ghersa, *Mod. Plast.*, **36**, 135–142, 212 (1958).
19. F. Bargellini, *Mod. Plast. (Milan)*, **28**, 372 (1962).
20. L. Audouin, B. Dalle, G. Metzger, and J. Verdu, *J. Appl. Polym. Sci.*,