# Effects of crystallinity on ageing phenomena in poly(vinyl chloride)

**C. Tsitsilianis, M. Tsapatsis and Ch. Economou**
*Department of Chemical Engineering, University of Patras, GR-26110, Patras, Greece*
*(Received 16 May 1988; revised 9 December 1988; accepted 17 February 1989)*

The physical ageing of poly(vinyl chloride) (PVC) is affected by the degree of crystallinity which can be induced by annealing of the sample at temperatures above $T_g$. Differential scanning calorimetry (d.s.c.) measurements showed that the enthalpy relaxation, induced by sub-$T_g$ annealing, of PVC samples with different crystallinity increases with increasing crystallization temperature ($T_c$). On the other hand, the enthalpy relaxation decreases with increasing crystallization time ($t_c$) at a given $T_c$. These observations cannot be attributed only to the overall crystallinity percentage, but they are attributable mainly to the entire structure of the amorphous phase which depends upon above-$T_g$ annealing conditions ($T_c$, $t_c$). The assumptions of different portions of the material crystallized at different $T_c$ and of decreasing extent of disturbed regions as $t_c$ increases seem to explain well the above findings. Solvent sorption experiments served to support our suggestions resulting from d.s.c. experiments.

**(Keywords: physical ageing; poly(vinyl chloride); enthalpy relaxation; crystallinity; annealing; d.s.c.)**

## INTRODUCTION

During the last decades a great deal of attention has been focused on the phenomenon of physical ageing in glassy amorphous polymers. It is well known that polymer glasses exist in a non-equilibrium state and for that reason significant changes in the physical properties of the polymer occur as it approaches equilibrium[1-4].

Annealing of amorphous polymers at temperatures $T_A$ near and below the glass transition temperature $T_g$, causes ageing phenomena which can be accomplished over a short time scale.

Sub–$T_g$ annealing affects a large number of the properties of the polymer, for example impact strength, Young's modulus and transport properties. Changes in these properties are governed by two major parameters, the annealing temperature $T_A$ and the annealing time $t_A$. It has been shown that the enthalpy relaxation $\Delta H_R$, which is measured by endothermic peaks observed on the $T_g$ area by differential thermal analysis (d.t.a), is an increasing linear function of log $t_A$ at a given $T_A$ (ref.2).

Semicrystalline polymers also undergo physical ageing which takes place in the amorphous phase of the material[3,5]. As has been demonstrated by Tant and Wilkes[5] the physical ageing of the amorphous regions of semicrystalline poly(ethylene terephthalate) (PET) affects the bulk properties of this material. Stress–strain and stress–relaxation experiments have demonstrated that physical ageing decreases with increasing degree of crystallinity. Moreover, the ageing rate was shown to decrease linearly with the percentage of crystallinity extrapolated to zero at 100% crystallinity.

Poly(vinyl chloride) (PVC) has been widely used as an amorphous glassy polymer for the study of the phenomenon of physical ageing[3,6-8]. Moreover, it has been shown that annealing of the polymer above the glass transition temperature, causes crystallization[6,9-11] which can be demonstrated by endotherms in d.s.c. experiments. This thermal-induced crystallinity can reach up to about 15%. In a recent paper, Ballard *et al.*[12] demonstrated that PVC does not form spherulites, and the crystalline lamellae, if present, have maximum thickness of about 25 to 30 Å and cannot form visible assemblies.

In this paper the influence of crystallinity (induced by annealng of the samples at temperatures $T_c$ above $T_g$) on the physical ageing of PVC induced by annealing at temperatures $T_A$ below $T_g$ has been studied. Using the above procedure we have examined well characterized PVC samples, which present structural differences (crystallinity and physical ageing) induced by different well controlled thermal treatments. Because similar structural changes could be induced during plastic processing (e.g. injection moulding), the study of their influence on the properties of the end product has a practical interest.

The main method which has been employed in this study is differential scanning calorimetry (d.s.c.) which allows the determination of the enthalpy relaxation corresponding to the ageing process. This method has been used for two reasons. Firstly, a thermogram can reveal the thermal history of the material, i.e. one endothermic peak on the $T_g$ area corresponding to the relaxation phenomena and another endothermic peak on the melting temperature of crystallites, $T_m$, corresponding to the crystallinity. Secondly, these phenomena can be distinguished and be studied separately.

## EXPERIMENTAL

### *Materials*

The polymer used in all experiments was a commercial suspension-polymerized PVC obtained by E.K.O. (Hellas). The average molecular weights of the polymer were determined by gel permeation chromatography (g.p.c.) in THF at 25°C, using a standard Waters g.p.c. apparatus. The $M_n = 36\,300$ and $M_W = 75\,500$ ($M_W/M_n = 2.1$). The polymer was obtained in white

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powder form and was used with 4% dibutyltin dilaurate as thermal stabilizer.

### *Film samples*

Films were prepared by compression moulding at 230°C under 5 000 psi pressure for 1–2 min and quenched to 0°C.

### *Powder samples*

Experiments were performed with samples in powder form. During thermal treatment the powder was placed into glass tubes under nitrogen atmosphere.

### *Annealing*

In order to assure a common thermal history, all samples were annealed at 200°C for 5 min and quenched to 0°C before any other thermal treatment. Subsequently, the samples were subjected to successive annealing according to the scheme.

$$T_0 \nearrow T_c(t_c) \searrow T_0 \nearrow T_A(t_A) \searrow T_0$$

where $T_0$ is 0°C, $T_c$ is the annealing temperature above $T_g$ in which the samples undergo crystallization, $t_c$ is the annealing time at $T_c$, $T_A$ is the annealing temperature at which the samples undergo physical ageing (enthalpy relaxation) and $t_A$ is the annealing time at $T_A$. After annealing at $T_c$ or $T_A$ the sample is quenched to 0°C.

### *Differential scanning calorimetry (d.s.c.)*

D.s.c. scans were carried out with films or powder samples of about 10 mg, under a nitrogen atmosphere, using a Du Pont 910 thermal analyser. The apparatus was calibrated with an indium standard. The heating rate was 20°C/min and the peak area was measured by an image analysis system (Konton).

### *Sorption properties*

Films with dimensions of 1.8 cm × 3.0 cm and thicknesses of 0.5 ± 0.05 mm with different thermal histories were used in sorption experiments. Each sample was immersed in liquid toluene at 30 ± 0.02°C. After specified periods of time the sample was removed from the toluene, placed between folds of tissue paper to remove excess toluene, weighed several times over in a period of minutes and reintroduced into the liquid. The weight of the film at each immersion time was obtained from graphical extrapolation to zero time after each removal from the solvent.

## RESULTS AND DISCUSSION

### *Differential thermal analysis*

In order to study the influence of crystallinity on the physical ageing phenomena it is necessary to determine the thermally induced crystallinity of PVC which depends on the nature of the material (e.g. syndiotacticity percentage)[10]. Samples having the same pre-annealing thermal histories were subjected to annealing above $T_g$ at different temperatures $T_c$ (between 110 and 160°C) and times $t_c$ (10–300 min). The enthalpy of fusion of crystallites, $\Delta H$ was calculated from d.s.c. thermograms by measuring the area of the endotherms from 90 to 217°C (*Figure 2*, curve a). The enthalpy of fusion, $\Delta H$, is given as a function of crystallization temperature $T_c$ for different annealing times $t_c$ in *Figure 1*. As is shown, $\Delta H$ passes through a maximum at 130–140°C in accordance with the results of Gray and Gilbert[10]. It must be mentioned here that the temperature of fusion of crystallites, $T_m$, depends on the annealing time, $t_c$. More precisely, at any $T_c$, $T_m - T_c = c$ where $c$ is positive and increases generally with $t_c$[6,10,11].

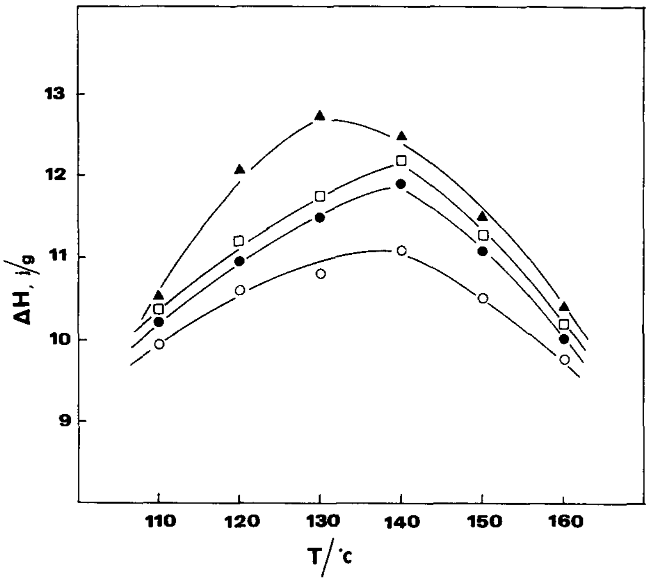

Figure 1 Enthalpy of fusion $\Delta H$ of crystallized PVC as a function of crystallization temperature, for different crystallization times: (○) 10 min; (●) 30 min, (□) 90 min; (▲) 120 min

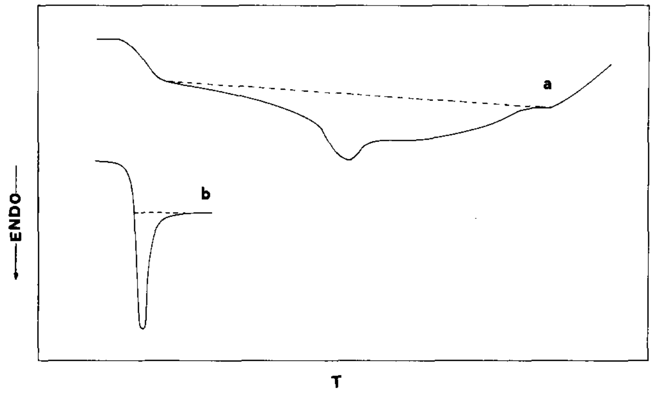

Figure 2 Example of the determination of (a) enthalpy of fusion of crystallites, $\Delta H$ and (b) enthalpy relaxation $\Delta H_R$

Subsequently, films with different crystallinities induced by above-$T_g$ annealing at different values of $T_c$ for 90 min, were subjected to sub-$T_g$ annealing at 66°C for different times $t_A$ in order to study the ageing phenomena. The enthalpy relaxation, $\Delta H_R$, was computed from d.s.c. thermograms by measuring the area of the endothermic peak enclosed between the d.s.c. trace and the extrapolation of the baseline established at temperatures above $T_g$ (*Figure 2*, curve b) and applying corrections according to the Bauwens method[13].

In *Figure 3* the enthalpy relaxation, $\Delta H_R$, is given as a function of the temperature $T_c$ (at which the sample undergoes crystallization) for various ageing times, $t_A$. The arrows indicate the $\Delta H_R$ of the untreated samples (those which have not been subjected to above-$T_g$

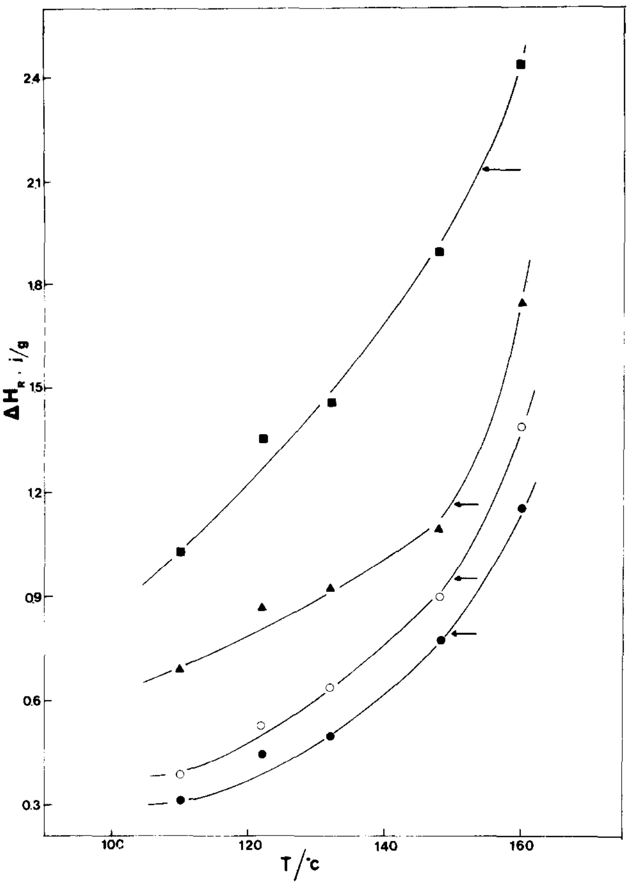

**Figure 3** Enthalpy relaxation $\Delta H_R$ of PVC with different crystallinities annealed at 66°C, as a function of crystallization temperature for different sub-$T_g$ annealing times: (●) 4 h; (○) 10 h; (▲) 33 h; (■) 48 h. The arrows indicate the $\Delta H_R$ of the untreated PVC

annealing present, nevertheless, a broad endotherm with $\Delta H = 9.6$ J/g). Two interesting results are observed in *Figure 3*. Firstly, the enthalpy relaxation $\Delta H_R$ increases monotonously with respect to $T_c$ at a given $t_A$ although crystallinity percentage presents a maximum for $T_c$ 130–140°C (see *Figure 1*). Secondly the $\Delta H_R$ of the sample crystallized at 158°C is higher than that of the untreated sample, although the crystallinity of the first is greater than that of the second. It is known that the relaxation effect (ageing) takes place in the amorphous phase of the material. One expects the curves in *Figure 3* to pass through a minimum at 140°C because at this crystallization temperature the material has the maximum crystallinity percentage (maximum $\Delta H$, see *Figure 1*), and therefore, the minimum glassy amorphous phase. It is apparent that the results cannot be explained in a simple quantitative manner, based only on the crystallinity percentage.

In order to prove that these results are not due to experimental error, as well as to study the influence of the crystallization time, $t_c$, a new cycle of experiments was performed. The samples were in powder form in an attempt to avoid possible orientations which can be induced during the moulding process. Samples crystallized at 132 and 158°C for different times $t_c$ (10 min, 5 h) were annealed at 66°C for several times, $t_A$. Typical thermograms of samples with different thermal histories are illustrated in *Figure 4*.

From this second series of experiments it is observed that the crystallinity behaviour of the powder form samples resembles that of the film samples, i.e. for a given $t_c$, $\Delta H(\text{untreated}) < \Delta H\ (T_c = 158°\text{C}) < \Delta H(T_c = 130°\text{C})$ or for a given $T_c$ $\Delta H(\text{untreated}) < \Delta H(t_c = 10\,\text{min}) < \Delta H(t_c = 5\,\text{h})$ (*Table 1*). The smaller values are perhaps due to the more difficult heat transfer in the powder samples. Moreover, comparing the endothermic peaks corresponding to the enthalpy of fusion of crystallites of all the samples crystallized at the same conditions ($T_c$, $t_c$), it was found that $\Delta H$ remains unaltered after the sub-$T_g$ annealing. The value is the same for all the samples compared. This provides support for the validity of the methods used to obtain the d.s.c. results and the thermal histories.

The enthalpy relaxation, $\Delta H_R$, as a function of the logarithm of the annealing time $t_A$, for samples of different crystallinities is plotted in *Figure 5*. The observed linear dependence of $\Delta H_R$ with log $t_A$ verifies that the ageing phenomena proceed in a similar manner in all samples. On the other hand, the differences in the slopes of the curves (rate of ageing) can be attributed to the different crystallinities of the material. Another aspect which has to be mentioned here, is that if we superimpose the two

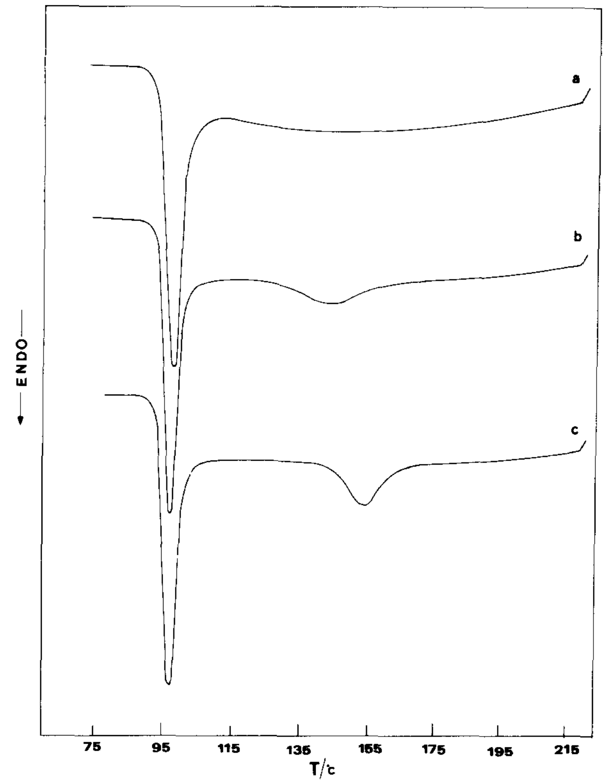

**Figure 4** D.s.c. scans of PVC annealed at 66°C for 243 h. Curve a untreated; curve b crystallized at 132°C for 10 min; curve c crystallized at 132°C for 5 h

**Table 1** Enthalpy of fusion for powder-form samples crystallized at different conditions

| $T_c$ (°C) | $t_c$ (min) | $\Delta H$ (J/g) |
|---|---|---|
| 130 | 10 | 5.2 |
| | 300 | 5.8 |
| 158 | 10 | 4.8 |
| | 300 | 5.3 |
| untreated | | 4.5 |

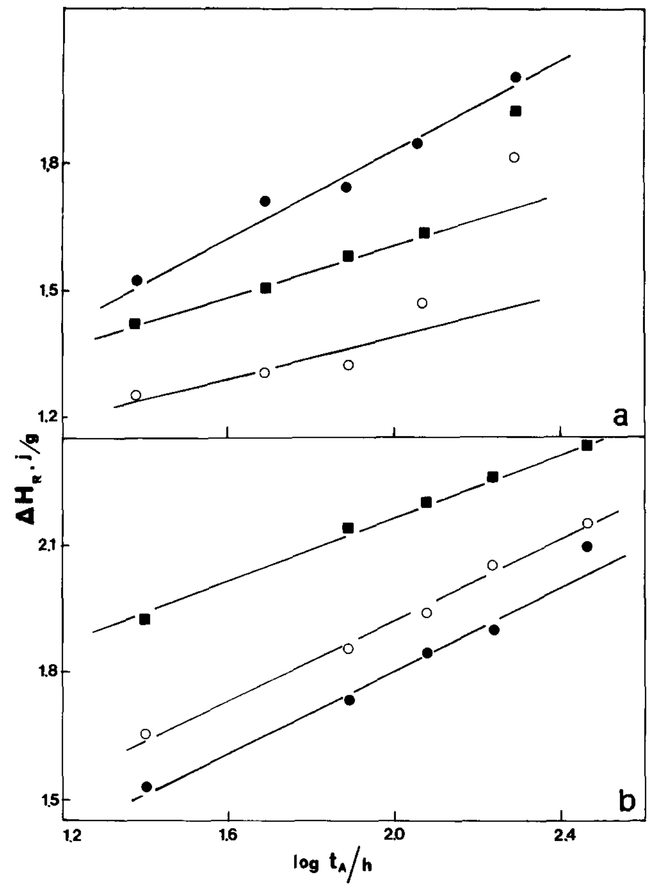

**Figure 5** Enthalpy relaxation $\Delta H_R$ as a function of log $t_A$ for PVC crystallized at (a) 132°C; (b) 158°C. (●) untreated; (○) $t_c = 10$ min; (■) $t_c = 5$ h

curves in *Figures 5a* and *b*, which correspond to the untreated PVC, we observe that they almost coincide. This strongly supports the d.s.c. results.

*Figure 5a* shows that the curve for the PVC crystallized at 132°C lies below the curve corresponding to the untreated PVC. In *Figure 5b* the curve for the PVC crystallized at 158°C lies above the curve of the untreated PVC. These results are in good agreement with those obtained with the film samples. Another interesting result is that the enthalpy relaxation, $\Delta H_R$, of the samples which have been crystallized at a given $T_c$ for $t_c = 10$ min is lower than the $\Delta H_R$ of the samples with $t_c = 5$ h. What one expects is that the PVC ($t_c = 10$ min), which contains a lower percentage of crystallinity (see *Table 1*), should undergo a more extensive physical ageing and therefore should have a higher $\Delta H_R$ than that of PVC ($t_c = 5$ h).

In order to explain the above results we must take into account the conditions ($T_c$, $t_c$) at which the crystallinity of PVC is formed and the type of crystallites formed under these conditions. The percentage of crystallinity (reflected on $\Delta H$) plays a role but cannot justify the observed influence of crystallinity on the ageing phenomena.

In order to correlate the crystallinity with the ageing phenomena, we consider the model of Struik[3] in which the ageing is directly related to segmental mobility or inversely related to the degree of packing. In semi-crystalline polymers, besides the crystalline regions (zero mobility) there are also the disturbed regions (reduced mobility) in the vicinity of the crystallites, at which the ageing phenomena are reduced[3].

Moreover Illers[6] suggested that in PVC different parts of the material crystallize at different crystallization temperatures. Thus, it seems that the ageing process must be affected by three factors: the crystallinity percentage; the extent of the disturbed regions, which depends on the size and the magnitude of crystallites; and the kind of segments bound in the crystallites.

In the case of samples subjected to crystallization for a given $t_c$ at various values of $T_c$, the observed behaviour can primarily be attributed to the kind of segments bound in the crystallites. Because $T_m$ depends on $T_c$, we can assume that at any $T_c$ different parts of the material are crystallized or recrystallized during the above-$T_g$ annealing. At low crystallization temperatures, the crystallites are formed from segments of large mobility (because the crystallites melt at low $T_m$). This means that the material disposes fewer parts of large mobility which are able to undergo physical ageing. On the contrary, at high crystallization temperatures, the crystallites are composed of low mobility segments (high $T_m$) allowing a more extensive ageing. Changes in crystallinity percentage affect the ageing process, but the ageing behaviour of PVC seems to be controlled mainly by the different kinds of segments bound in the crystallites. The changes in size and magnitude of crystallites and therefore in size of disturbed regions with respect to the crystallization temperature, are expected to depend more on crystallization time and not on the crystallization temperature. Thus, they are less pronounced and contribute less to the ageing phenomena.

In the case of the samples subjected to crystallization at a given $T_c$ for different times $t_c$, the observed behaviour can be attributed to the extent of the disturbed regions. In fact, at $t_c = 10$ min the crystallites are very small in size and very numerous. Thus they cause more extensive disturbed regions. On the contrary, at $t_c = 5$ h recrystallization occurs[9] and the size of crystallites increases while their number decreases. This leads to a smaller extension of disturbed regions. Moreover, the crystallites are composed of segments with different mobilities ($T_m$ of PVC ($t_c = 10$ min) is lower than $T_m$ of PVC ($t_c = 5$ h); see also *Figure 4*) contributing in an analogous manner, as mentioned in the preceding paragraph, to the observed ageing behaviour. Finally, it has been observed that the enthalpy relaxation of PVC crystallized at 158°C is greater than that of the untreated PVC.

As we have observed, the pre-treatment of the material at 200°C for 3 min cannot destroy the existing crystallinity because it is re-introduced on cooling[10]. Owing to the short crystallization time untreated PVC contains very small crystallites and an extended area of disturbed regions around them. On the other hand crystallization at high temperatures (158°C) leads to the formation of crystallites constituted of low mobility segments which do not in any way contribute to the ageing process. Furthermore, the increase in crystallinity induced by annealing at 158°C is small compared with the crystallinity of the untreated sample. The final result seems to be that the undisturbed regions of PVC crystallized at 158°C, which present a high segmental mobility available to physical ageing, are more extensive than those of untreated PVC, which is highly disturbed.

It could be concluded that the influence of crystallinity on the physical ageing of PVC can mainly be attributed to the entire structure of the material, including the crystalline phase and the disturbed and undisturbed

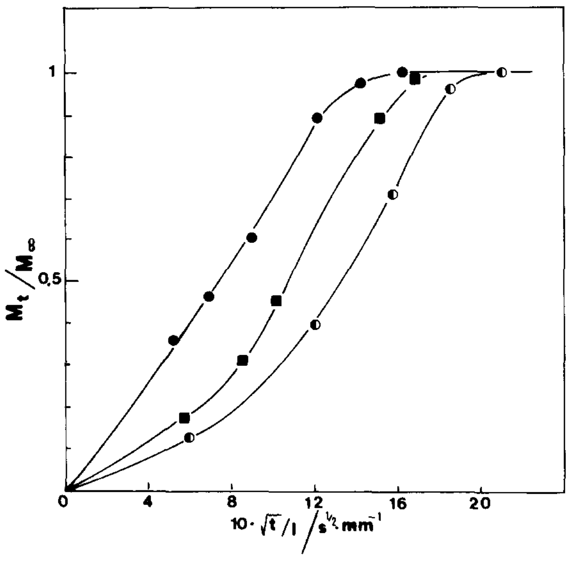

**Figure 6** Solvent sorption curves for PVC crystallized for 5 h at (●) 158°C; (■) 132°C; (◐) 110°C

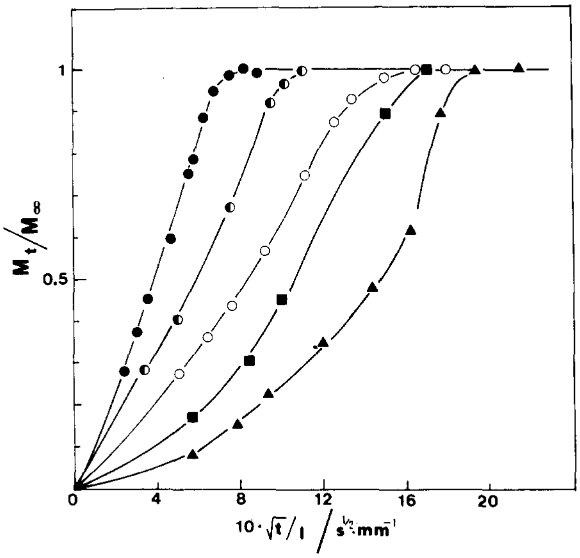

**Figure 7** Solvent sorption curves for PVC with different thermal histories: (●) untreated; (◐) $T_A=66$°C (24 h); (○) $T_A=66$°C (48 h); (■) $T_c=132$°C (5 h); (▲) $T_c=132$°C (5 h)/$T_A=66$°C (24 h)

**Table 2** Maximum gain (%) of PVC samples crystallized at different conditions

| $T_c$ (°C) | $t_c$ (h) | $\Delta H$ (J/g) | Maximum gain percent |
|---|---|---|---|
| 110 | 5 | 11.1 | 52 |
| 132 | 5 | 13.0 | 50 |
| 158 | 5 | 10.7 | 58.5 |

regions of the amorphous phase, and less to the percentage of induced crystallinity.

### *Solvent sorption measurements*

In order to corroborate the above results solvent sorption experiments were performed. This technique was employed because the sorption of small molecules into the polymer matrix proceeds mainly in the region of high segmental mobility or low degree of packing. Consequently, crystallization of the material induced by annealing is expected to influence the sorption in a similar manner as it influences the ageing phenomena. In addition, it is interesting to examine the changes occurring on the solvent sorption behaviour after above $T_g$ and sub-$T_g$ thermal treatment of the material.

Sorption measurements were carried out in toluene for PVC samples with different thermal histories. *Figure 6* represents solvent sorption curves (fractional uptake $M_t/M_\infty$ *versus* square root of diffusion time over thickness $t^{1/2}/l$) for three different PVC samples subjected to annealing at $T_c=110$, 132 and 158°C for 5 h, respectively. This result is in good agreement with the previous d.s.c. results. If the only difference between the samples crystallized at different temperatures was the degree of crystallinity, the rate of sorptions would present a minimum for the highest crystallinity sample corresponding to $T_c=132$°C. However, this is not the case. The regions presenting high segmental mobility available to rapid sorption, increase as the crystallization temperature increases. This is the determining factor for the sorption rate, not the differences in crystallinity percentage between the samples.

Moreover, it is known that the toluene maximum gain (%) of the samples is affected by the percentage of crystallinity (i.e. on $\Delta H$). More precisely, the maximum gain is inversely related to the enthalpy of fusion, $\Delta H$. The results demonstrated in *Table 2* are consistent with the above predictions.

Solvent sorption curves for five PVC samples with differential thermal histories (mentioned on the figure) are illustrated in *Figure 7*. It can be seen that the rate of solvent sorption is reduced when the material undergoes annealing above or below $T_g$ in agreement with the results of Gray and Gilbert[14]. Moreover, the sample annealed successively at 132°C for 5 h and at 66°C for 24 h presents a more pronounced decrease in the sorption rate due to crystallization and volume relaxation of the material. Consequently, we can say that crystallization and physical ageing also influence the sorption properties of the polymer.

## CONCLUSIONS

The physical ageing of PVC is strongly affected by the existence of crystallinity which can be induced by above-$T_g$ annealing procedures. The enthalpy relaxation of PVC samples with different crystallinities increases with increasing crystallization temperature $T_c$, at constant crystallization times $t_c$. In addition, the enthalpy relaxation of the samples crystallized at a given $T_c$ for 10 min is lower than that of the samples crystallized for 5 h. The above findings cannot be attributed only to the overall percentage of crystallinity which is reflected in the enthalpy of fusion, but also to the entire structure of the material. It seems that the quality of crystallites produced under certain conditions ($T_c$, $t_c$) influences the structure of the amorphous phase (i.e. the extent of disturbed regions, as well as the segmental mobility of undisturbed regions) which is responsible for the ageing phenomena. Solvent sorption experiments corroborate the above assumptions.

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