Glass transition and physical ageing in plasticized poly(vinyl chloride)

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Several samples of poly(vinyl chloride) both unplasticized and plasticized with dioctyl phthalate, have been examined by differential scanning calorimetry. It was observed that, while the glass transition temperature T_g decreased as expected with increasing plasticizer content, a small portion of the sample appeared to be resistant to the plasticizer. This was manifest in the appearance of a second T_g corresponding to the unplasticized sample which remained unaffected by addition of plasticizer. The ageing behaviour of the samples was also examined using enthalpy relaxation measurements and it was observed that the presence of plasticizer accelerates the ageing process, probably due to the fact that there is greater mobility of the chains in the plasticized samples.

(Keywords: poly(vinyl chloride); glass transition temperature; plasticization; enthalpy relaxation; ageing)

INTRODUCTION

Suspension and mass polymerization of poly(vinyl chloride), PVC, produces free-flowing particles of approximately 100 μm size. Inside them, other smaller particles, of approximately 1 μm size, called primary particles, can be seen[1,2]. Using different experimental techniques[3-5] the existence of still smaller structures, microdomains, of around 100 Å size, has been demonstrated, but it is not clear at present how the crystalline phase (~5–10%[6]) can be related to them.

During the processing, the primary particles may disappear if the processing temperature is high enough[7,8] but microdomains have also been observed in processed PVC[3] as well as in plasticized PVC[4]. It has been suggested that the plasticizer is only absorbed in the intermicrodomain region of amorphous PVC[9].

The aim of this work is the study, using differential scanning calorimetry, of the influence of this complex morphology on the glass transition and physical ageing of plasticized PVC.

EXPERIMENTAL

The unplasticized PVC compound, supplied by Aiscondel S.A., contained the following additives: lead-based stabilizer 3.2%, stearic acid 0.2%, titanium dioxide 0.5%, carbon black 0.04%. The average molecular weight was 120000 ± 5000, measured at 298 K, with a Waters liquid chromatograph model ALC/GPC equipped with a U6K injector, a set of 4 μm Styragel columns, and an R-401 refractive index detector. Tetrahydrofuran was used as eluent.

Samples in the shape of sheets approximately 0.2 mm thick were prepared by calendering the polymer at 463 K for 10 min.

Samples of plasticized PVC with different plasticizer contents were prepared by dry mixing the PVC with dioctyl phthalate (DOP) and calendering at 463 K for 10 min.

Experimental tests were carried out in the Department of Chemistry at the University of Stirling. A Perkin–Elmer differential scanning calorimeter, model DSC2, was used and the data were collected using an Apple II computer by means of a 12-bit analogue–digital interface. Six points per degree were collected but only one datum point per degree is represented in the figures.

The experiments on unaged samples were carried out with the following thermal history. The sample was held at 400 K for 10 min, thus eliminating the effect of previous thermal histories. It was then cooled at 40 K min^{-1} until the temperature T_0 selected for the start of the scan was reached. The values of T_0 for the different samples are given in *Table 1*. The sample was then heated at 20 K min^{-1} from T_0 to 400 K. Data were collected only on heating. All the thermal treatments were carried out in the calorimeter. The thermal history corresponding to ageing experiments will be described below.

In this work only one unplasticized sample was used

Table 1 Start temperature of the scan and glass transition temperature of the samples

	DOP content (%)					
	0	2	5	10	15	20
T_0 (K)	300	300	280	280	275	275
T_g (K)	354	347	337	321	311	304.5

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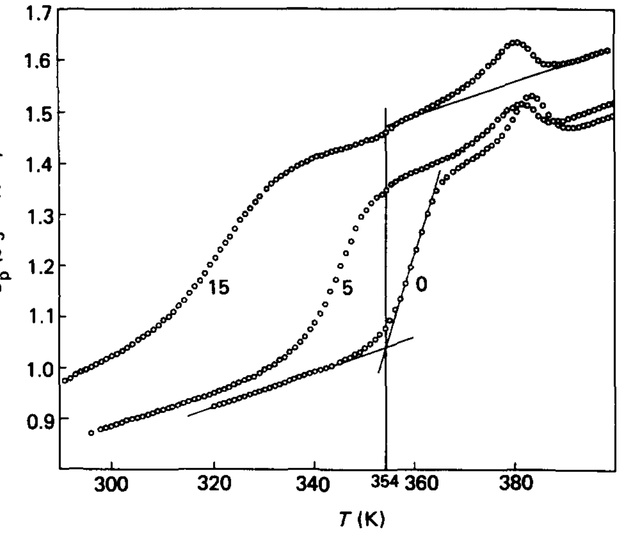

Figure 1 Specific heat of unplasticized and plasticized PVC as a function of temperature. The content of DOP (wt %) of the sample is indicated on each curve

and one each with the following contents of DOP: 2, 5, 10, 15 and 20 wt %.

With the purpose of increasing the precision of the specific heat measurements an empty pan scan and a standard sapphire scan were run corresponding to each PVC sample scan. The specific heat of the PVC sample was then calculated using the equation:

$$C_{ps} = \frac{D_s}{D_z}\frac{m_z}{m_s}C_{pz}$$

D_s and D_z are the heat fluxes measured on the PVC sample and on the sapphire sample respectively, m_s and m_z are the weights of the PVC and sapphire samples, both about 25 mg, and C_{pz} is the specific heat of the sapphire.

RESULTS AND DISCUSSION

Unaged samples

The scan corresponding to an unplasticized and unaged PVC sample shows the glass transition in the temperature range between 345 and 370 K (*Figure 1*). The extrapolated glass transition temperature T_g is 354 K, calculated as shown in *Figure 1*. The peak in $C_p(T)$ appearing between 370 and 390 K, above the glass transition, is representative of a first-order thermodynamic transition.

In the plasticized samples it can be observed, as expected[10,11], that the glass transition broadens and is shifted towards lower temperatures (*Figures 1* and *2*). The values of the extrapolated T_g as a function of the DOP content are shown in *Table 1*. In addition, in samples containing more than 2 wt % DOP a second glass transition can be seen, at 354 K, with an increment in C_p of around 0.01 J g^{-1} K^{-1} (*Figures 1* and *2*), which does not change when the amount of plasticizer in the sample increases.

This second glass transition, which occurs at the same temperature as in the unplasticized sample, supports the hypothesis that two different amorphous phases exist in the plasticized PVC. This also suggests the existence of two amorphous phases in unplasticized PVC, both with the same T_g, one of which does not absorb plasticizer. When the plasticizer is added, the T_g of the solvated phase diminishes and the two different glass transitions can be observed. This conclusion is also supported by the results of Foldes *et al.*[12] who found, using thermally stimulated depolarization current (TSDC) measurements, that the characteristic peak of the α dielectric relaxation (closely related to the glass transition) of unplasticized PVC is split into two peaks in plasticized PVC, one of them at the same temperature as that in the unplasticized PVC and the other one at a lower temperature.

These two phases in amorphous PVC can be explained by assuming that the plasticizer is not able to penetrate the microdomains mentioned earlier.

In recent work, Beirnes and Burns[13] have reported two glass transitions in PVC plasticized with DOP but at a different temperature and with both transitions changing temperature as the plasticizer content changes. They have also offered a different interpretation to that given in this work. These two transitions have not been observed in our results probably because the DOP contents of our samples are not as high.

In unplasticized samples a peak also appears in $C_p(T)$ at temperatures ranging between 360 and 390 K (*Figures 1* and *2*). In samples containing 10, 15 or 20 % DOP it is possible to determine that there is no C_p increment associated with this transition. It can then be ascribed to the melting of crystals formed at low temperatures. This differs from the interpretation by Bair and Warren[11] who proposed that this transition was a second glass transition occurring at a temperature higher than in the unplasticized PVC. This led them to conclude that this second glass transition was due to syndiotactic sequences in the chain backbone.

The temperature of the maximum of $C_p(T)$ associated with this transition appears between 2.5 and 5 K below that corresponding to the unplasticized sample, but it is not possible to find a monotonic dependence of the temperature of the maximum with the plasticizer content. This is ascribed to differences in the crystallization kinetics of the different samples.

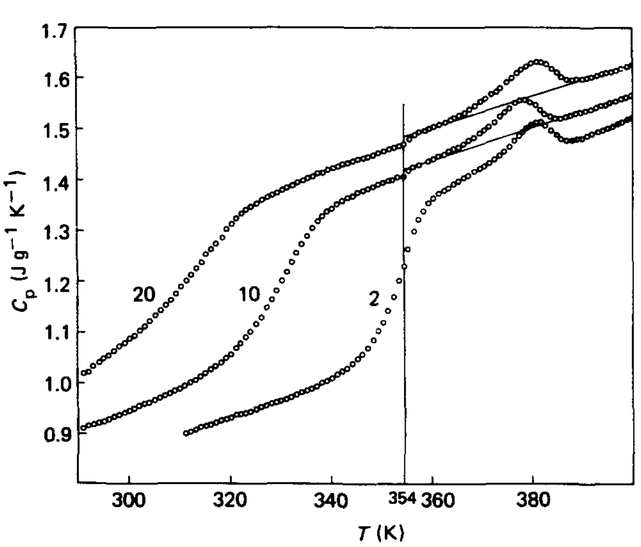

Figure 2 Temperature dependence of specific heat for plasticized PVC. The DOP content (wt %) is shown on each curve

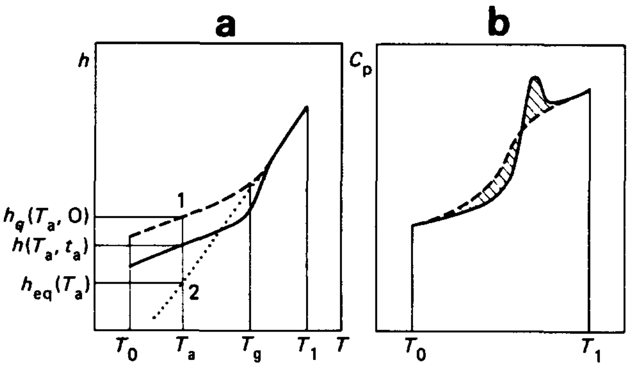

Figure 3 Schematic diagram of (a) enthalpy and (b) specific heat measured on heating an aged sample (full curves). The reference scan is represented as broken curves

Physical ageing in plasticized and unplasticized PVC

The physical ageing process in amorphous polymers is defined as the isothermal process which the material undergoes to approach thermodynamic equilibrium at a temperature below the glass transition temperature, i.e. in the glassy state. During this process the specific enthalpy diminishes continuously with time. When the glass has been formed by cooling the material from a temperature T_1 above T_g to another one T_a below T_g, at a cooling rate q, the value of the enthalpy when the temperature T_a is reached is called hereafter $h_q(T_a,0)$ (state 1 in *Figure 3a*). The equilibrium state at temperatures corresponding to the glassy state cannot easily be reached experimentally, even at only a few degrees below T_g. The value of the enthalpy corresponding to equilibrium can only be taken hypothetically as the extrapolation of the $h(T)$ curve determined at temperatures above T_g (and therefore in equilibrium). This theoretical equilibrium curve has been drawn in *Figure 3a* as a dotted line. Thus the theoretical equilibrium value of enthalpy at the temperature T_a is $h_{eq}(T_a)$ (state 2 in *Figure 3a*). The ageing process at the temperature T_a takes the material from the state 1 to 2 and its kinetics will be defined by the function $h(T_a,t_a)$, the ageing time t_a being the time elapsed after the temperature T_a was reached in the cooling stage. One can also use the function $\Delta h(T_a,t_a)=h_q(T_a,0)-h(T_a,t_a)$ called the enthalpy lost due to ageing.

The measurement of this latter parameter was carried out using a differential scanning calorimeter following the method described by Lagasse[14]. The ageing experiments were performed with the following thermal history: the sample was held at 400 K for 10 min, then cooled to the temperature T_a at a cooling rate q, held at this temperature during a time t_a and cooled again at the same cooling rate until the temperature T_0 was reached. The measuring scans were then carried out at a heating rate q' between T_0 and 400 K. The result of this kind of experiment is similar to that drawn in *Figure 3b* with a full curve. A test on an unaged sample, also called the reference scan, entailed cooling at a rate q from 400 K to T_0 and the measuring scan was then carried out at the heating rate q' from T_0 to 400 K. The result is represented by the broken curve of *Figure 3b*. It can be easily shown that the shaded area in *Figure 3b* is equal to the difference $h_q(T_a,0)-h(T_a,t_a)$ if the curves $h(T)$ corresponding to the two experiments are parallel between T_0 and T_a.

The cooling rate used in this work was $40\,\mathrm{K\,min^{-1}}$ because it is the highest that the temperature controller of the DSC2 is able to control. The heating rate was $20\,\mathrm{K\,min^{-1}}$. The reference scan was repeated five times and an average of these measurements was used. Sometimes, especially in the experiments with the shortest ageing times, a reference scan measured immediately after the one corresponding to the aged sample was used in order to obtain a higher reproducibility in the experimental conditions.

The kinetics of the ageing process in unplasticized PVC samples, as well as in samples containing 5 and 10% DOP, were studied. The ageing temperature T_a in each sample was 8 K below its T_g, thus allowing a comparison of the results for different samples. The values of T_a are given in *Table 2*.

There is no complete agreement about the correct way to calculate the glass transition temperature from calorimetric measurements in order to use it as a reference value in comparing the ageing process of different polymers. In this work the onset temperature of the glass transition region was used because of its agreement with the literature value[15] and because of what has been previously discussed in the section related to the unaged samples. Nevertheless, a tentative test was carried out comparing the ageing process of the unplasticized sample and the one containing 10% DOP, at an ageing temperature 13.5 K below the temperature of the midpoint of the rise of the $C_p(T)$ curve in the transition region. The result of this test was not very different from that shown in this work and all the conclusions would remain unchanged if the glass transition temperature was calculated in the latter way.

The representation of the enthalpy lost against the ageing time for the three samples is given in *Figure 4*, showing a significant influence of the plasticizer on the ageing. Several mathematical models have been proposed to analyse the process phenomenologically[16–18], which assume the existence of a recovery time distribution which is a function of the departure from equilibrium. Nevertheless, because of the kind of experimental results available in this work it is preferable to use simpler models. Cowie and Ferguson[19] have successfully used an equation similar to that of Williams and Watts[20]:

$$\Delta h(T_a,t_a)=\Delta h_{\infty \mathrm{WW}}\left\{1-\exp\left[-\left(\frac{t}{t_c}\right)^{\beta}\right]\right\} \qquad (1)$$

which was used to fit the experimental results in this work. In *Figure 4* the curves shown are the best fit found for each sample and in *Table 2* the corresponding constants are given. The value of $\Delta h_{\infty \mathrm{WW}}$ represents the difference in enthalpy between the initial and final states of the ageing

Table 2 Parameters characterizing the physical ageing process

	DOP content (%)		
	0	5	10
T_a (K)	346	329	313
ΔC_p ($\mathrm{J\,g^{-1}\,K^{-1}}$)	0.304	0.316	0.278
$\Delta h_{\infty \mathrm{th}}$ ($\mathrm{J\,g^{-1}}$)	2.444	2.519	2.254
$\Delta h_{\infty \mathrm{WW}}$ ($\mathrm{J\,g^{-1}}$)	1.469	1.600	1.677
t_c (min)	232	520	367
β	0.3	0.33	0.43
τ_0	7.153	6.711	5.117
s	−6.13	−5.18	−3.46

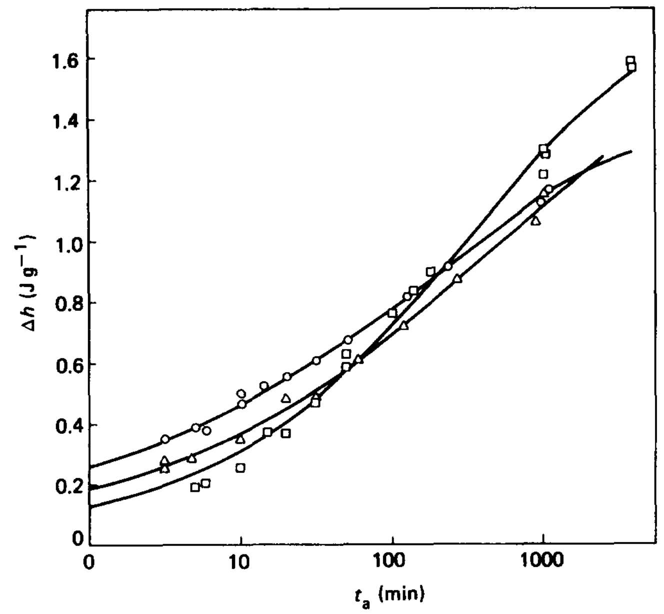

Figure 4 Enthalpy lost due to ageing for the unplasticized PVC sample (○) and the samples containing 5% (△) and 10% (□) DOP. The full curves are the best fits of the experimental results found with equation (1)

process. This value can be compared with that calculated from the $C_p(T)$ curve corresponding to the reference scan, called hereafter $\Delta h_{\infty th}$. If it is assumed that the curves $h_g(T)$ and $h_l(T)$, corresponding to the glass and the liquid respectively, intersect each other at the temperature T_g as represented in *Figure 3a*, one has:

$$\Delta h_{\infty th} = h_q(T_a,0) - h_{eq}(T_a) = \int_{T_a}^{T_g} (C_{pl} - C_{pg})\,\mathrm{d}T \qquad (2)$$

where $C_{pl}(T)$ and $C_{pg}(T)$ are the specific heat of the liquid and the glass respectively.

It is difficult to determine the curve $C_{pl}(T)$ because of the presence of the melting peak which in unplasticized samples overlaps the glass transition. The results obtained on samples with the highest content of plasticizer show that it is possible to adjust the $C_{pl}(T)$ curve at temperatures above the range of the melting peak. In this way both glass transitions are included in the $\Delta h_{\infty th}$ calculation in plasticized samples. The value of $\Delta h_{\infty th}$ calculated from these $C_{pl}(T)$ data must be used only as indicative of the order of magnitude because of the imprecision of the extrapolation of $C_{pl}(T)$ in the temperature range of the glass transition. In fact, the value of $\Delta h_{\infty th}$ for the sample with 5% DOP is, unexpectedly, higher than in the unplasticized sample (*Table 2*). In the three samples the value of $\Delta h_{\infty WW}$ calculated from equation (1) is significantly lower than the theoretical one.

The parameter β seems to be the most significant when comparing the ageing process of the three samples. A high value of β indicates a faster approach to equilibrium. It can be concluded that the plasticizer accelerates the ageing by increasing the mobility of the chain backbone segments, which seem to be responsible for the process[21].

A very interesting parameter in the study of ageing is the effective recovery time which can be used with different experimental techniques[16,22-24]. If the relaxation function $\phi(t_a)$ is defined by the equation:

$$\Delta h(T_a,t_a) = \Delta h_\infty[1-\phi(t_a)] \qquad (3)$$

the effective recovery time τ_{eff} is given by:

$$\frac{\mathrm{d}\phi(t_a)}{\mathrm{d}t_a} = -\frac{\phi(t_a)}{\tau_{eff}(\phi)} \qquad (4)$$

and it depends both on the ageing temperature and on the value of $\phi(t_a)$. A linear dependence has been found between $\log \tau_{eff}$ and ϕ when ϕ is neither near 0 or 1. *Figure 5* shows the values of τ_{eff} and *Table 2* gives the parameters for the fit of $\log \tau_{eff}$ vs. ϕ expressed by the linear relationship:

$$\log \tau_{eff} = \tau_0 + s\phi \qquad (5)$$

The line corresponding to the sample containing 5% DOP is shifted to the right, probably due to an excessively high value of $\Delta h_{\infty th}$ in this sample. The slope s diminishes

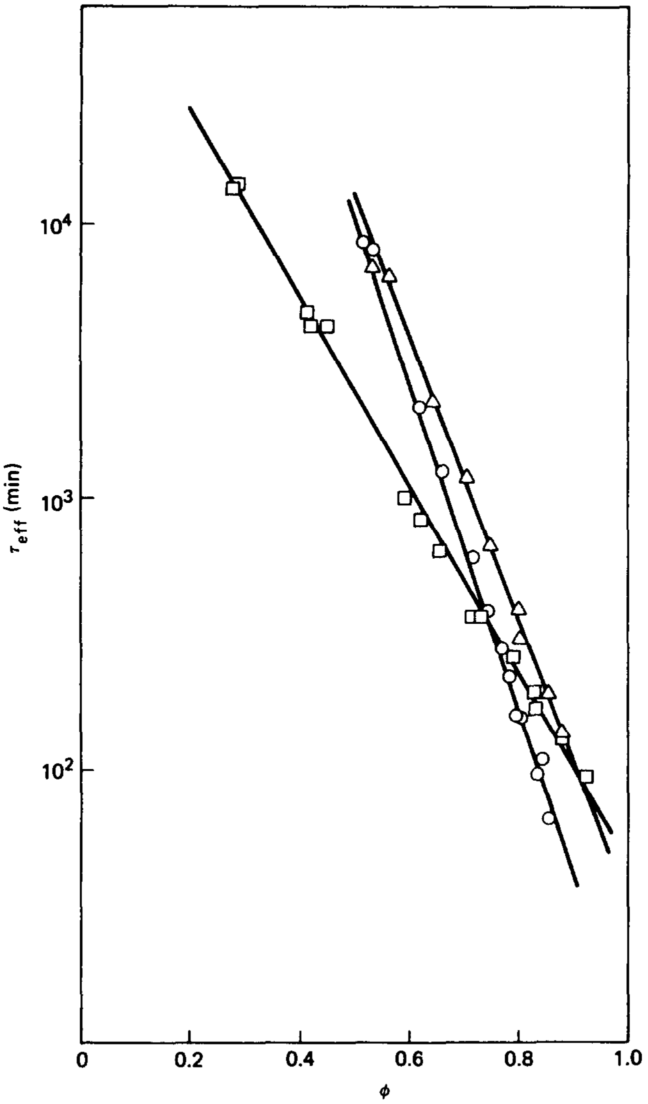

Figure 5 Effective recovery times of the ageing process. Symbols as in *Figure 4*

continuously as the plasticizer content increases, the interpretation of this fact being the same as for the β parameter of equation (1).

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