

Antiplasticization of poly (vinyl chloride) in relation to thermal ageing and non-linear viscoelastic behaviour

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(Received 22 July 1977; revised 24 October 1977)

Up to the present the phenomenon of antiplasticization has been investigated mainly by means of dynamic mechanical tests or short term, constant straining rate, tensile tests. This paper reports an experimental study on the creep response of poly(vinyl chloride) compositions containing respectively 0 and 10 phr tricresyl phosphate, together with the influence of thermal ageing. The results suggest that the phenomenon of antiplasticization is time, temperature and stress dependent, i.e. above certain critical values, the phenomenon assumes all the typical characteristics of normal plasticization. Whereas for unplasticized compositions, both the elastic and the time dependent component of the compliance are affected by thermal ageing throughout the whole range of retardation times, those containing the additive exhibit a reduction in the values of $L(\ln \lambda)$ only at the upper end of the spectrum.

INTRODUCTION

Although the term antiplasticization has only been used quite recently¹ the phenomenon, in its essence, has been known for a long time. Brous and Semon², for instance, in 1935 reported an anomalous behaviour in poly(vinyl chloride) compositions containing up to 18% tricresyl phosphate with respect to tensile strength: an unexpected maximum was observed at about 10% plasticizer. Later in 1945, Buckman³ reported corresponding maximum and minimum values for the hardness and elongation to break, respectively, at the same concentration. The softening point on the other hand decreased monotonically with increasing plasticizer concentration.

These early observations have laid down the foundations of the present knowledge of antiplasticization, while the contributions that have followed⁴⁻¹¹ served only to confirm the occurrence of the phenomenon or at the most to reveal certain additional features. The advent of dynamic mechanical tests has thrown some light on the underlying mechanisms of the phenomenon¹²⁻²⁵ but little attention has been given to the effects of thermal and stress history on the long term deformational behaviour.

Questions arising from considerations of rate processes

The above issue raises the following questions: (a) does the antiplasticizer accelerate the process of thermal hardening experienced when ageing the polymer just below the main glass transition temperature?; (b) Does the phenomenon of antiplasticization vanish as a result of stress activation in a manner similar to the softening effect caused by increasing the temperature?

On the basis of Eyring's theory one could visualize a situation in which the stress accelerates molecular relaxations by reducing the activation energy barriers, i.e.:

$$\lambda_i = \frac{\lambda_0}{\exp(-\Delta H/RT)\sinh(v\sigma/RT)} \quad (1)$$

where λ_i is the retardation time of each individual component of the overall deformational process; λ_0 is a constant for the material, dependent on the number of molecular species involved for each relaxation; ΔH is the thermal activation energy of the process; v is the activation volume of the deformations and σ is the excitation stress.

This equation reduces to:

$$\lambda_i = \lambda'_0 \exp\left(\frac{\Delta H - v\sigma}{RT}\right) \quad (2)$$

The above hypothesis implies that the stress does not affect the elastic component of the deformational process (i.e. since this is time independent it cannot participate in the rate process) hence one can utilize linear models, such as the standard linear solid, to take into account the non-linearity resulting from stress activation. The time-dependent compliance in this case would be represented by the familiar equation:

$$D(t) = D_0 + \int_{-\infty}^{\infty} L(\ln \lambda) [1 - \exp(-t/\lambda)] d(\ln \lambda) \quad (3)$$

where $L(\ln \lambda)$ is the 'distribution of retardation times' defined as:

$$L(\ln \lambda) = D_i \cdot \lambda_i \approx \left. \frac{dD(t)}{d(\ln t)} \right|_{t = \lambda_i} \quad (4)$$

Table 1 Poly(vinyl chloride) compositions

Type of raw materials	Description of raw materials	Formulations	
		I	II
Suspension homopolymer	Viscosity index (ISO R174) = 87	100	100
Tricresyl phosphate	Mixture of <i>o</i> -, <i>m</i> - and <i>p</i> -isomers. MW = 368	—	10
Stabilizer	Dibutyltin maleate	2.5	2.5
Lubricant	Stearic acid	2.0	2.0

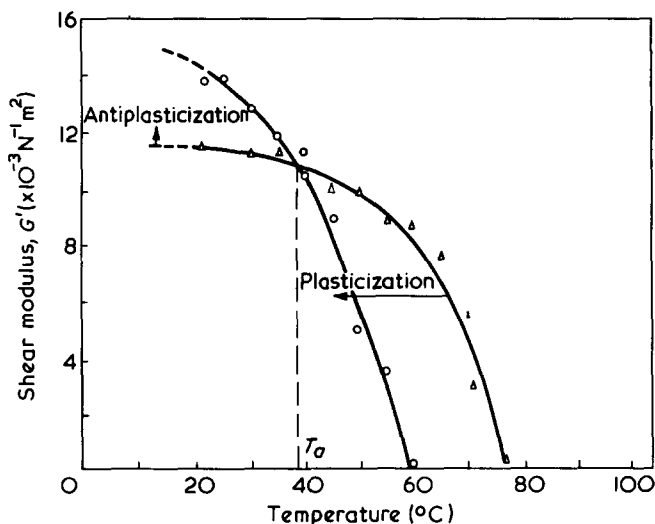


Figure 1 Antiplasticization/plasticization transition in dynamic mechanical tests. Δ , Unplasticized PVC; \circ , PVC + 10 phr tricresyl phosphate

One can therefore quantify the effect of stress activation by taking the slope of the compliance vs. $\log(\text{time})$ curve at various time intervals and stress levels.

On the basis of the above considerations the antiplasticizer may not only affect the elastic component (as indicated by dynamic tests) but could also have a pronounced effect on the activation volume which would in turn alter the time-dependent response at any given stress level.

EXPERIMENTAL

Sample preparation

For the purpose of the investigation, compositions based on poly(vinyl chloride) were selected and 10 phr tricresyl phosphate were used to produce an adequate degree of antiplasticization. The complete formulations are shown in Table 1.

The components were premixed cold in a high speed powder mixer and melt blended at 165°C in a Ko-Kneader compounding extruder. The extrudates were presheeted on a two roll mill and compression moulded in a water-cooled press at 170°C into circular discs. These were then aged for three months in polyethylene bags immersed in a water bath at 60°C. At the end of this period two additional samples were prepared and together with the aged samples were stored in a refrigerator.

Evaluation of the viscoelastic characteristics

Specimens were machined from the moulded discs and tested using the following techniques and conditions:

(a) free vibration (Nonius) torsion pendulum, over the temperature range 20°–110°C; (b) tensile creep at 20°C for periods of up to 18 h and nominal stress levels of 16–23 MN/m²; (c) cantilever beam bending creep at 30°C for periods up to 3 months and nominal stress levels up to 5 MN/m².

DISCUSSION

The well established low temperature antiplasticization phenomenon followed by normal plasticization at higher temperatures is clearly revealed by means of dynamic mechanical tests from the measurements of the modulus as a function of temperature (Figure 1). The loss factor, calculated from the decay of the oscillations of a torsion pendulum, however, fails to reveal the transition from antiplasticization to plasticization (Figure 2). This association of antiplasticization with the elastic component of the deformation process is also borne out from low stress creep data in Figure 3 where the above-mentioned transition is shown to occur only at relatively long times, i.e. when the retarded response becomes operative. The results in Figure 4 are in agreement with the findings of Turner on thermal ageing of rigid PVC. The divergence of the curves in Figure

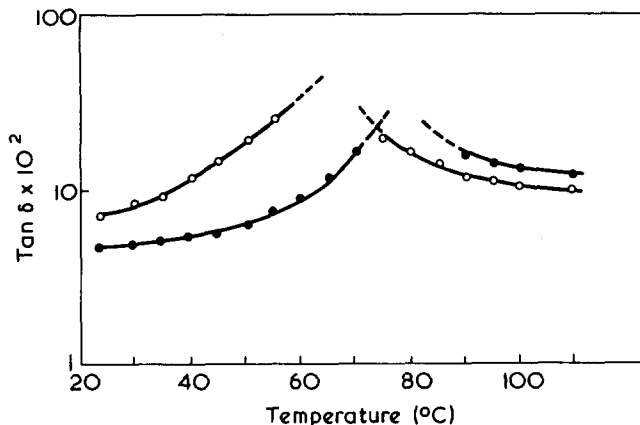


Figure 2 Effect of plasticizer on dynamic mechanical damping. \bullet , Unplasticized PVC; \circ , PVC + 10 phr tricresyl phosphate

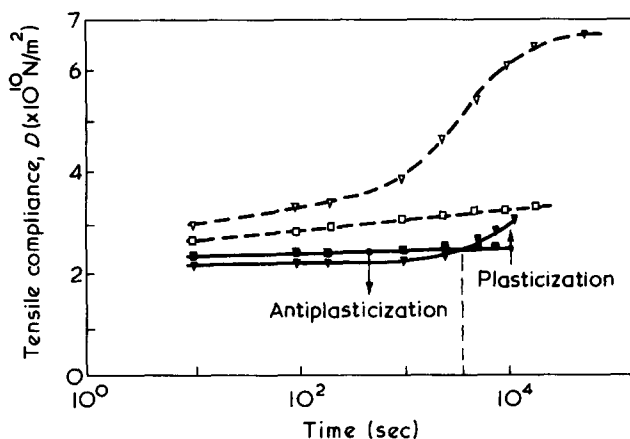


Figure 3 Effect of plasticizer on creep behaviour of PVC compositions (unaged samples). \blacksquare , \square , Unplasticized PVC; \blacktriangledown , \triangledown , PVC + 10 phr tricresyl phosphate; \blacktriangledown , \triangledown , nominal stress = 16 MN/m²; \triangledown , \square , nominal stress = 25 MN/m²

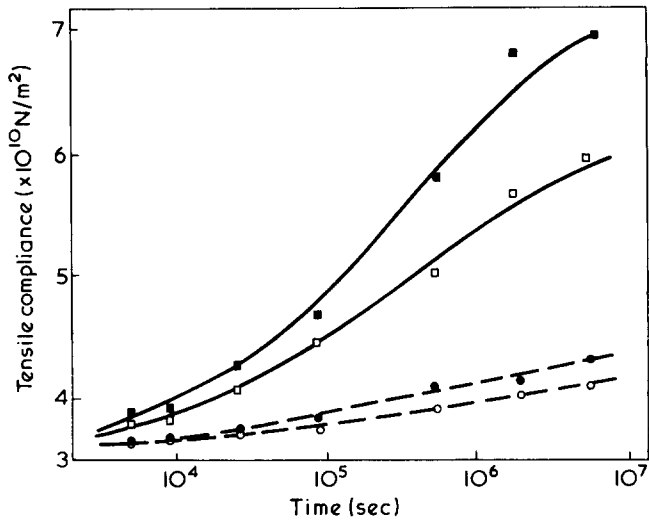


Figure 4 Effect of thermal ageing on creep behaviour of unplasticized PVC. □, ■, Unaged specimens; ○, ●, aged specimens; □, ○, nominal stress = $2.5 \times 10^6 \text{ N/m}^2$; ■, ●, nominal stress = $5.0 \times 10^6 \text{ N/m}^2$

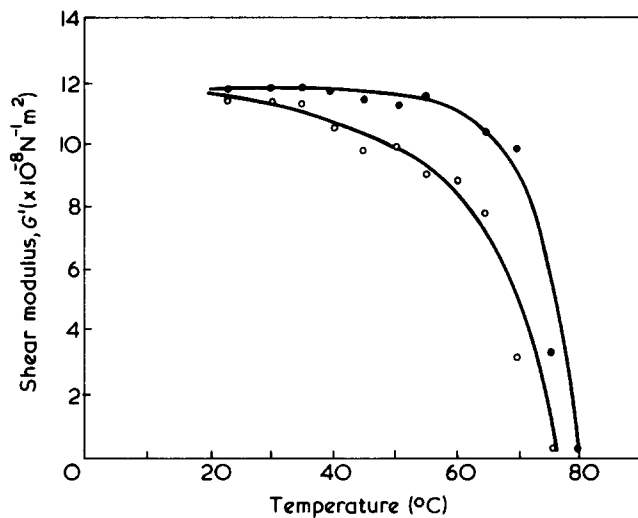


Figure 5 Effect of thermal ageing on dynamic modulus of unplasticized PVC. ○, Unaged samples; ●, aged samples

5 with increasing temperature bears further witness to the distinct features of thermal ageing of glassy polymers.

In the case of the PVC composition containing the anti-plasticizer, on the other hand, the dynamic modulus and loss factor is not affected by the thermal treatment (Figures 6 and 7). An appreciable difference, however, is noted in the creep results (Figure 8). The order of magnitude of the time-dependent strain softening behaviour is even greater than that observed for the unplasticized material. From the creep results it can be clearly seen that the additive also increases the degree of non-linearity of the deformational process, resulting from stress activation effects. Although, for the cantilever bending experiments, the true extent of this effect may be falsified by the errors arising from the use of classical elasticity theory.

CONCLUSIONS

In the light of the above results it can be inferred that anti-plasticization is a phenomenon which reduces the comp-

liance or increases the modulus of polymers only at low temperatures, short times and small stresses, i.e. under conditions in which there is a prevailing contribution by the elastic response due to the increase in intermolecular forces.

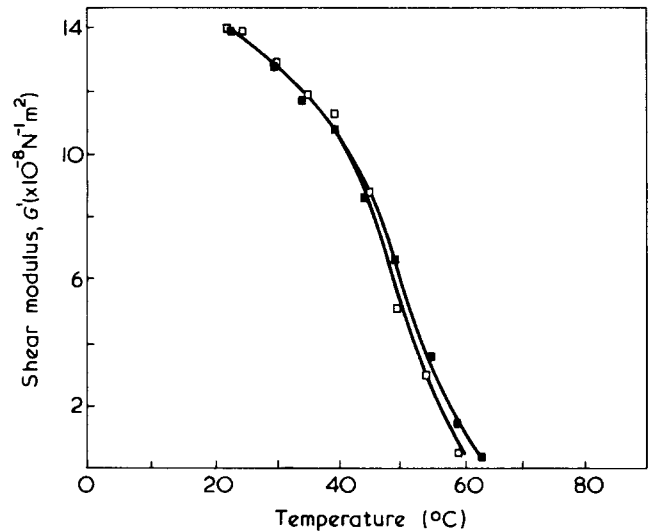


Figure 6 Effect of thermal ageing on dynamic modulus of PVC compositions containing 10 phr tricresyl phosphate □, Unaged samples; ■, aged samples

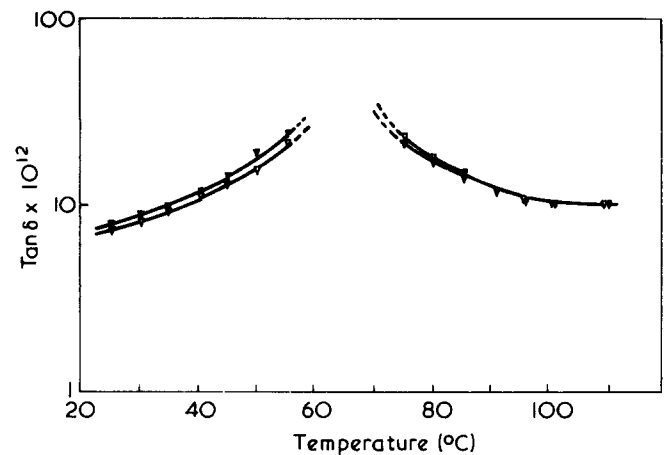


Figure 7 Effect of thermal ageing on dynamic losses of PVC compositions containing 10 phr tricresyl phosphate. ▼, Unaged samples; ▽, aged samples

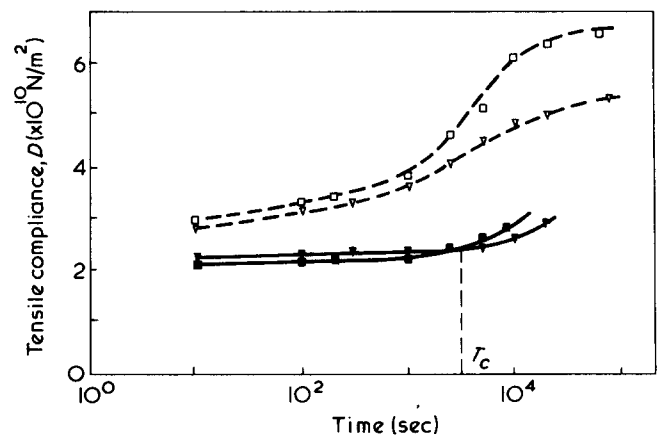


Figure 8 Effect of thermal ageing on creep behaviour of PVC compositions containing 10 phr tricresyl phosphate. □, ■, Unaged samples; ▽, ▼, aged samples; □, ▽, nominal stress = 25 MN/m^2 ; ■, ▼, nominal stress = 16 MN/m^2

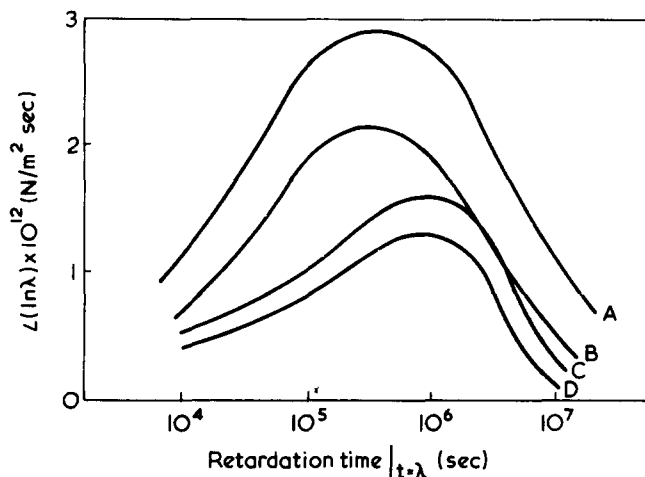


Figure 9 Effects of thermal ageing on distribution of retardation time of PVC compositions containing 10 phr tricresyl phosphate. A, B, Unaged specimens; C, D, aged specimens; B, D, nominal stress = 2 MN/m²; A, C, nominal stress = 4 MN/m²

On the other hand, the phenomenon vanishes under conditions which involve segmental rotations within the molecular framework (i.e. for large strains, high temperatures and long times) as a result of the decrease in energy barriers brought about by the activation effects of the excitation stresses, and assumes all the characteristics of normal plasticization. Furthermore, thermal ageing does not affect the elastic component of antiplasticized compositions (quite unlike the case of the unplasticized polymer) but decreases dramatically the values of $L(\ln\lambda)$ at longer elapsed times and reduces the time over which the major relaxations take place (Figure 9).

ACKNOWLEDGEMENTS

The author wishes to thank Mr L. M. Welsh for granting permission for the use of the results of his undergraduate project.

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