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# Viscoelastic modelling and strain-rate behaviour of plasticized poly(vinyl chloride)

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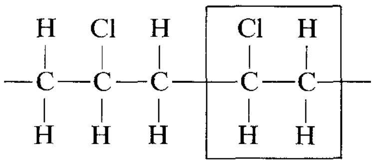
The effect of four different types of plasticizers and four strain-rates on the tensile behaviour of poly(vinyl chloride) (PVC) has been studied. di(2-ethylhexyl phthalate), benzyl butyl phthalate, epoxidized soyabean oil and chloroparaffin were mixed at different ratios and were used as plasticizers in concentration levels of up to 77% of the PVC weight. The plasticized and unplasticized PVC were processed into sheets by compression moulding. Tensile tests were conducted at different strain rates. It was found that tensile modulus increases with increasing strain rate while it decreases with increasing plasticizer concentration. The rate of variation of tensile modulus either as a function of strain rate and/or the plasticizer concentration was, in all cases, dependent on the mixing ratio of the different types of plasticizers. Assuming the material to be a linearly viscoelastic one, a simple viscoelastic model along with a least-squares-based computer procedure was applied which enabled us to fit the experimentally obtained curves with the respective theoretical predictions as well as to study the strain-rate effect on the relaxation spectrum, $H(\tau)$, of the material under consideration.

## 1. Introduction

The range of usage of PVC is very wide. Success in any one of the various applications is, however, vitally dependent on careful attention to compound formulation, processing conditions and to product design. PVC is a linear thermoplastic polymer with a chemical structure of the form



$$-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\boxed{\underset{\mathrm{H}}{\overset{\mathrm{Cl}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}}-$$

The presence of the chlorine atom causes an increase in the interchain attraction and hence an increase in the hardness and stiffness of the polymer.

There are many materials which are suitable plasticizers for PVC. They have similar solubility parameters to PVC and are also weak proton acceptors. These have too high a molecular weight and too large a molecular size to dissolve the polymer at room temperature, but they may be incorporated by mixing at elevated temperatures to give mixtures stable at room temperature. It appears that differences between liquids in their plasticizing behaviour are due to differences in the degree of interaction between polymer and plasticizer. There are a number of materials which are very similar in their effect on PVC compounds, but for economic reasons are most commonly used. The epoxidized oils and related materials are good plasticizers and very light stabilizers in PVC compounds.

A number of materials exist which are not in themselves plasticizers for PVC because of their very limited compatibility with the polymer, but in conjuction with a true plasticizer a mixture is achieved which has a reasonable compatibility. Commercial extenders, as these materials are called, are cheaper than plasticizers and can often be used to replace up to one-third of the plasticizer without serious adverse effects on the properties of the compound. These commonly employed types of extender are: (1) chlorinated paraffin waxes, (2) chlorinated liquid paraffinic fractions, and (3) oil extracts. It is obvious that the range of possible formulations based on PVC and related copolymers is very wide indeed. For each end-use the requirements must be carefully considered and a formulation devised that will give a compound of adequate properties at the lowest cost.

Because of the wide range of possible formulations it is difficult to make generalizations about the properties of PVC compounds. Mechanical properties are considerably affected by the type and amount of plasticizer. The role of plasticizer is, on the one hand, that of breaking the monotony of the configuration, that is "unwelding" the crystalline portions, and on the other hand, that of neutralizing the cohesive forces by removing the polar groups. Accordingly, with an increase in the quantity of plasticizer the compound becomes more flexible and less resilient. Finally, for a truly dissolving plasticizer we obtain a solution. The plasticized polyvinyl chloride compounds are then a solution of polymer in the liquid plasticizer. These must then be compatible, meaning that they must be carriers of molecular groups not presenting a marked repulsion in the presence of the polar groups of the polymer.

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The plasticizers may be of the type of dibasic esters. In cases where alcohols containing benzyl groups, as in the case of benzyl butyl phthalate (BBP), are used, the esters produced have a tendency to promote hardening and discoloration of compounds during exposure to sunlight. On the contrary, when aliphatic groups predominate (at least two or three), as is the case with di(2-ethylhexyl phthalate) (DOP), plasticizing action and stability are excellent.

Chlorinated paraffins, when incorporated into unstabilized poly(vinyl chloride) compositions, cause a rapid decrease in properties. The use of appropriate stabilizer, on the other hand, yields excellent results.

Discussion of the mechanism by which the plasticizer alters the properties of poly(vinyl chloride) has been given previously [1–3], the effects being interpreted in terms of altering the crystalline structure of this polymer. That the addition of plasticizer decreases the degree of crystallinity is quite likely, because the action of a compatible plasticizer is as a solvent, and any crystalline phases would tend to be less stable in the presence of solvent. However, according to Taylor and Tobolsky [4], PVC has a structure which is semicrystalline in nature, the crystallites being small enough to act as cross-links. Moreover, according to the same authors, the action of plasticizers on PVC is similar to their effect on completely amorphous polymers, but the crystallites remain stable under the action of plasticizer.

In the present work, the plasticizing effect of several mixtures of plasticizers on the viscoelastic behaviour of plasticized PVC was investigated. The strain-rate effect on the relaxation spectrum of the material under consideration was studied by means of a simple viscoelastic model along with a computer procedure.

## 2. Experimental procedure

### 2.1. Materials

The polymers and the plasticized samples were supplied by A. G. Petzetakis, S. A. Hellenic Plastics Industry. Table I gives the types and concentrations of plasticizers for all the five different compositions used in the present study are given. The plasticizers used were: (1) di(2-ethylhexyl phthalate) (DOP), (2) epoxidized soyabean oil (EPSO), (3) benzyl butyl phthalate (BBP) and (4) chloroparaffin. The physical properties of these plasticizers are given in Table II. The PVC was stabilized either with 0.9% by weight of Ba–Cd (Types 1, 3 and 5) and/or with 0.9% by weight of Ba–Cd–Zn stabilizer (Types 2 and 4).

TABLE I PVC compositions

| Plasticizer type | Type 1 | Type 2 | Type 3 | Type 4 | Type 5 |
|---|---|---|---|---|---|
| DOP | 29 | 36 | 40 | 50 | 50 |
| BBP | – | 5 | – | 20 | 10 |
| EPSO | – | 4 | – | 5 | – |
| Cl-52 | 11 | – | 17 | – | 17 |
| Total | 40 | 45 | 57 | 75 | 77 |

TABLE II Physical properties of plasticizers

| Type | $\eta$ (cP) | Refractive index | Molecular weight | Density ($g\,cm^{-3}$) |
|---|---|---|---|---|
| DOP | 80–85 | 1.486 | 390.6 | 0.986 |
| BBP | 55–65 | 1.540 | 312.0 | 1.115 |
| EPSO | 500 | 1.473 | 945.0 | 0.995 |
| Cl-52 | 9–19 | – | 400–500 | 1.23–1.26 |

### 2.2. Processing

The S-PVC (with a *k*-value of 70) and the stabilizers were mixed thoroughly in a mixer at 60 °C for 20 min. The plasticizers were then added according to the required concentration, hand-mixed, and then thoroughly mixed in a two-roll mill at 165 °C and then compressed at 150 °C and 3 MPa into a sheet of dimensions 200 mm × 200 mm × 3 mm. The sheets were cut to the appropriate dimensions of the desired test specimens and then machined to the exact dimensions using a routing machine.

### 2.3. Tensile tests

Tensile measurements were carried out with a conventional Instron-type tester at room temperature. The specimens were tested in four different rates of extension (2, 5, 10 and 20 mm $\text{min}^{-1}$). Five different types of specimens (shown in Table I) were used in order to study the effect of concentration and type of plasticizer on the viscoelastic behaviour of materials under investigation. Ten specimens for each composition were tested and the results correspond to their arithmetic mean value. Next, in order to understand and predict the viscoelastic behaviour of the plasticized PVC material, a simple viscoelastic model along with a computer procedure has been applied.

## 3. Viscoelastic modelling

### 3.1. Wiechert model

If we now consider *n* Maxwell elements in parallel plus an equilibrium spring, then we have the so-called Wiechert model. This model is shown in Fig. 1. If this model is considered to be subjected to a constant strain-rate test, then the total stress, $\sigma$, is equal to the sum of stresses developed on the individual elements. That is

$$\sigma = \sigma_e + \sum_{i=1}^{n} \sigma_i \tag{1}$$

and the total strain, $\varepsilon$, is given by

$$\varepsilon = C\,t \tag{2}$$

where $C$ is the constant strain rate.

On the other hand, the stress $\sigma_i$ developed in each Maxwell element is given by

$$\sigma_i = \tau_i m_i \left(1 - e^{-t/\tau_i}\right) C \tag{3}$$

Combining Equations 1 and 3, the total stress, $\sigma(t)$, is given by

$$\sigma(t) = \sigma_e + \sum_{i=1}^{n} \tau_i m_i \left(1 - e^{-t/\tau_i}\right) C \tag{4}$$

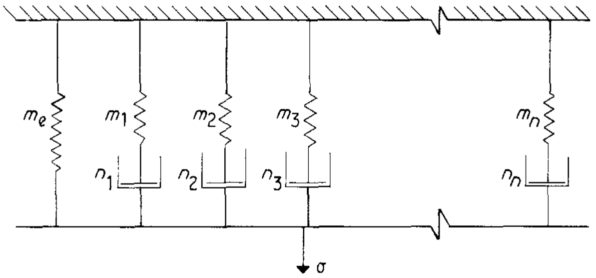

*Figure 1* The proposed viscoelastic model.

where

$$\sigma_e = m_e C t \tag{5}$$

Corresponding to each element's relaxation time, $\tau_i$, there is a definite spring constant, $m_i$, and a viscosity, $\eta_i$. The relaxation time, $\tau_i$, of the $i$th element is

$$\tau_i = \eta_i/m_i \tag{6}$$

Thus, one can associate or postulate a function

$$m_i = m_i(\eta_j) = m_i(\tau_j) \tag{7}$$

that becomes continuous as the number of elements increases without bound. A convenient form is found to be

$$m_i = [H(\tau_i)/\tau_i]\Delta_i\tau \tag{8}$$

where $\Delta_i\tau$ is the $i$th increment in relaxation time.

Assuming an infinite array of Maxwell elements (i.e. $n \to \infty$ and $\Delta_i\tau \to 0$), Equation 4 becomes

$$\sigma(t) = m_e R t + \int_0^\infty H(\tau)\,(1 - e^{-t/\tau})\,C\,d\tau \tag{9}$$

in which $H(\tau)$ is known as the "relaxation spectrum". Thus, instead of having to determine an infinite number of experimental constants $m_i$ and $\eta_i$, the problem has been traded for one of determining a suitable function $H(\tau)$. In the present case, the assumed form for $H(\tau)$ is

$$H(\tau) = (\tau_o/\tau)^n e^{-\tau_o/\tau} \tag{10}$$

so that upon substitution into Equation 9, there results

$$\sigma(t) = m_e C t + \int_0^\infty (\tau_o/\tau)^n e^{-\tau_o/\tau}(1 - e^{-t/\tau})\,C\,d\tau \tag{11}$$

The result of the above integration, is

$$\sigma(t) = \left[m_e t + \Gamma(n-1)\left(\tau_o - \frac{\tau_o}{(1 + t/\tau_o)^{n-1}}\right)\right] C \tag{12}$$

where $\tau_o$ depends on the temperature of the experiment.

Fig. 2 shows a typical stress–time curve with constant strain rate, $C$. At short time, $t \to 0$, the stress tends to zero, while for $t \to \infty$ there is a linear variation of $\sigma(t)$ and this is consistent with Equation 11. More precisely, from this relation one may observe that for $t \to \infty$, $\sigma(t) \to m_e C t$, i.e. $\sigma(t)$ is a linear function of time. In addition, we may observe that

$$\left.\frac{d\sigma(t)}{dt}\right|_{t\to\infty} = m_e C \tag{13}$$

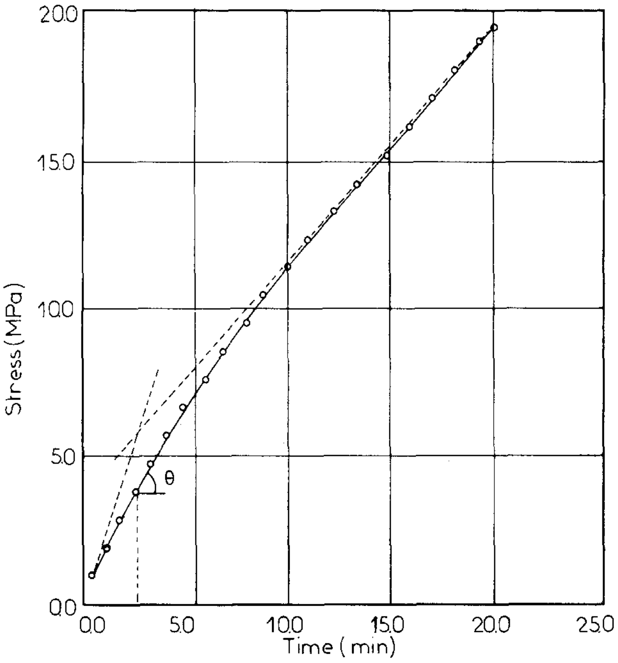

*Figure 2* A typical stress–strain curve from which the parameter $m_e$ can be evaluated. (○) Experimental points, $\tan\theta = n$.

Thus, for a given $C$, it is possible for $m_e$ to be evaluated from the slope of the linear part of the stress–time curve.

Using the above model, we shall try to describe the effect of plasticizer and strain-rate on the viscoelastic behaviour of PVC. The procedure is as follows: first, from the slope of the linear part of the stress–time curve and for a given $C$, we may determine the value of $m_e$. Next, the parameter $n$ can be determined as the slope of the stress–time curve through the transition region between glassy and rubbery behaviour, and finally $\tau_o$ can be determined through a repetitive computer procedure which minimizes the sum of differences between experimental values and theoretical predictions.

## 4. Results and discussion

Stress–strain curves at various strain rates were obtained for each material tested. All tests were performed at room temperature ( ~ 22 °C). A typical set of curves for specimens with 75% plasticizer content is shown in Fig. 3. The curves are plotted as stress calculated on the basis of the original cross-section, against engineering strain. Stress calculated on the basis of the original cross-section can be converted into stress based on the actual cross-section by multiplying by the principal extension ratio. This conversion is based on the assumption that Poisson's ratio is 0.5, which is true for unfilled rubber-like materials. Each curve represents the average of three curves obtained under identical conditions. In all cases, the scatter from test to test was essentially negligible and the curves thus represent the actual behaviour. The strain rates quoted are rounded to one significant digit because the tests are performed at constant machine crosshead velocity. The actual velocity of the ends of the specimen is somewhat different due to the compliance of the machine and loading attachments. Note

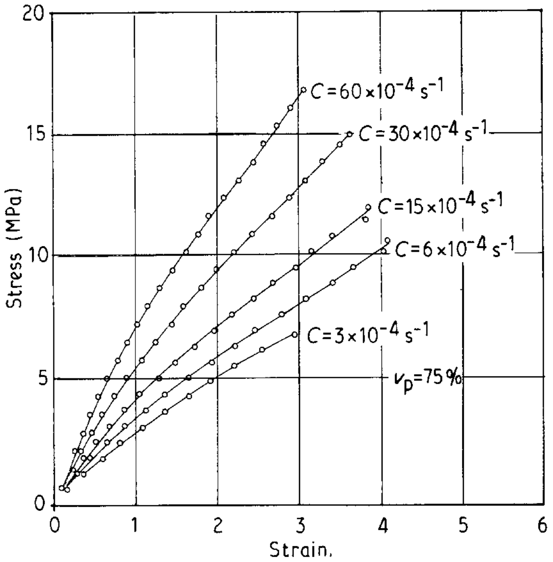

*Figure 3* Stress–strain curves measured at different strain rates for specimens with 75% plasticizer content.

further that, for small strains, the relation between specimen strain and displacement is also nonlinear. It is thus misleading to quote specimen strain rate to an accuracy greater than one significant digit.

The use of small specimens to obtain a stress–strain curve and the indirect determination of strain from relative specimen grip-displacement measurements makes the accuracy of the strain values no better than ± 5%. On the other hand, the use of identical specimens for tests at all strain-rates and the identical manner of calculating strains from grip-displacement measurements in each test makes the comparison of data at various strain rates much more reliable.

From the stress–strain curves obtained in the present investigation, Fig. 3, the effect of strain rate on the tensile behaviour of plasticized PVC is clear. Constant strain rate testing appears to be better suited for differentiating between viscoelastic materials which could or could not be fitted with the simple linear models. Also it is clear that plasticized PVC not only displays time and rate effects but also substantial behaviour as well. Perhaps it would be as well to point out here that one might be led to a conclusion that plasticized PVC is nonlinear in stress and strain from a casual glance at the data of Fig. 3. However, the data for each curve of Fig. 3 really represent a stress–time variation for constant strain-rate. A similar behaviour would be observed for stress–strain–strain rate response if the material were linear. A true stress–strain diagram for a linear material would be, in fact, linear, if the stress were plotted against strain from a series of creep or relaxation tests [5].

Plasticizers are compounded with poly(vinyl chloride) primarily to develop the desired physical properties. Two variables of concern are the kind of plasticizer used and its concentration. The temperature ranges over which the final product will be used, and also other environmental and processing factors, will also influence the choice and concentration of plasticizer.

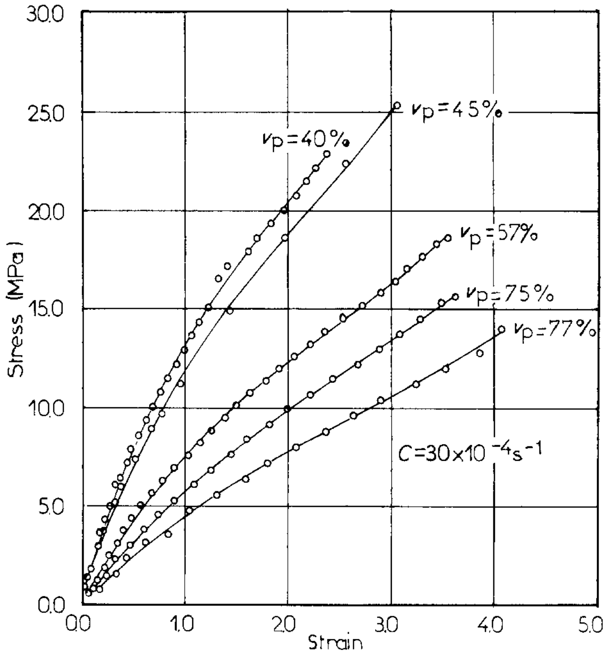

*Figure 4* Stress–strain curves for different plasticizer content and a constant strain rate.

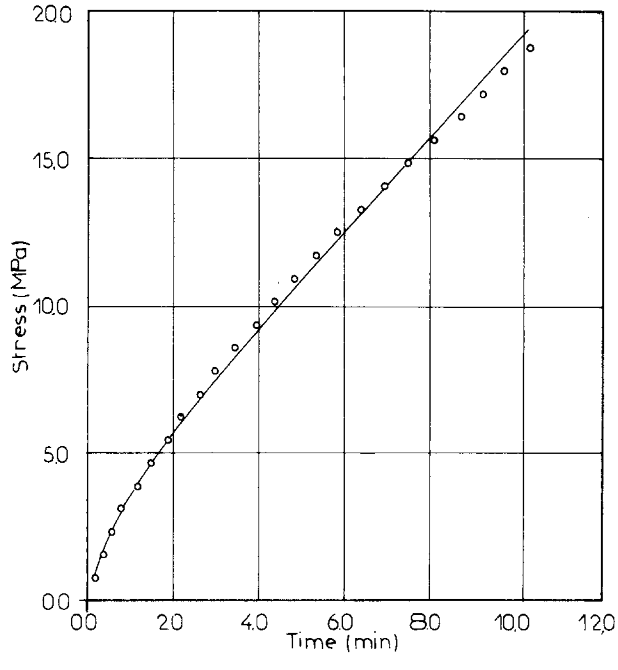

*Figure 5* Comparison between (○) experimental results and (——) theoretical predictions for the variation of stress with time. $C = 60 \times 10^{-4} s^{-1}$.

For most resin–plasticizer combinations at room temperature, a plasticizer threshold concentration must be passed before the normal plasticizer effects are observed on physical properties [6].

In the usual range of concentrations, the addition of 20% plasticizer makes the resin more flexible, reduces the modulus and tensile strength, and gives greater elongation.

In Fig. 4, stress–strain curves are plotted for different plasticizer content and for constant strain rate, $C = 30 \times 10^{-4} s^{-1}$. It may be observed that that behaviour considerably depends on the amount of plasticizer.

Fig. 5 shows experimental points as well as theoretical predictions for the variation of stress with time. As it may be observed, there is a good agreement between theory and experiment.

The variation of the elastic modulus, as calculated from the initial linear part of the corresponding stress–strain curves, versus strain rate for different plasticizer content is shown in Fig. 6. It is clear that for low concentrations, a high rate sensitivity is observed while for high concentrations the elastic modulus remains unaffected from the strain rate. This kind of behaviour is better shown in Fig. 7 where the variation of the elastic modulus is plotted against plasticizer concentration and for constant strain rate $C = 6 \times 10^{-4}\,s^{-1}$. From this figure we may observe that there is a continuous decrease in modulus as the plasticizer content increases. The same behaviour was observed for all strain rates applied in the present investigation.

Many types of mechanical models have been used extensively in the characterization of linear viscoelastic materials [7–12]. All the models make use of some

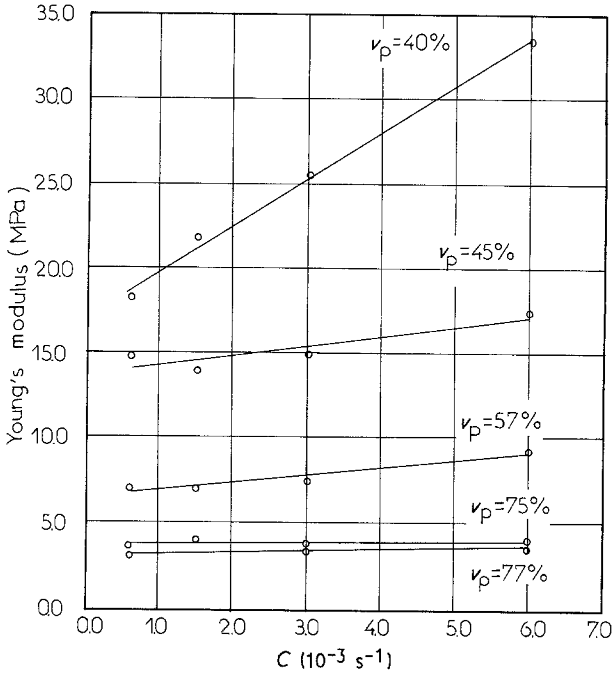

*Figure 6* Variation of the elastic modulus as a function of strain rate and for different plasticizer content.

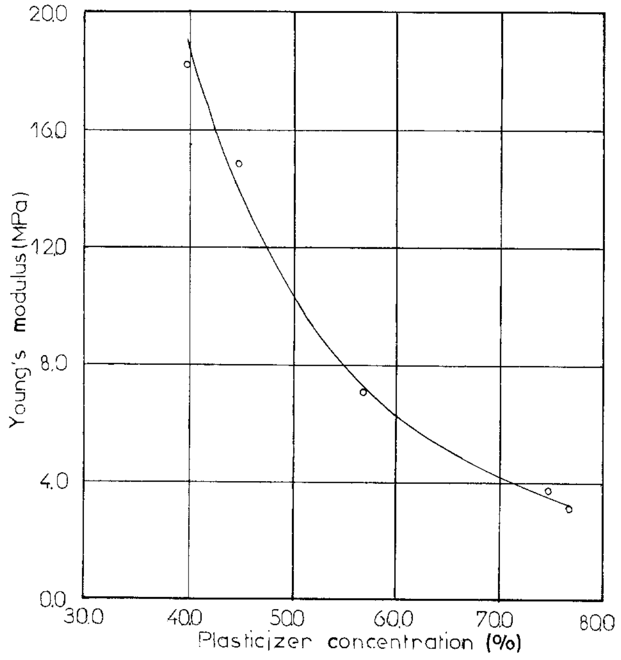

*Figure 7* Variation of the elastic modulus as a function of plasticizer concentration and for a constant strain rate, $C = 6 \times 10^{-4}\,s^{-1}$.

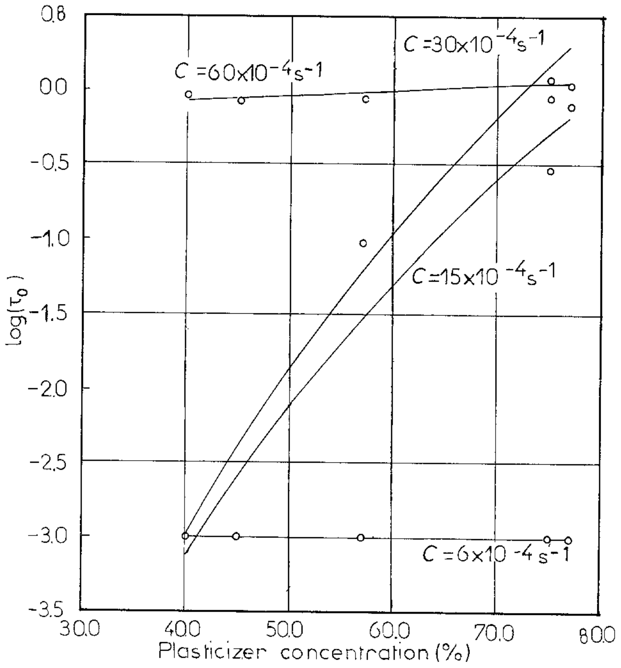

*Figure 8* Variation of log $\tau_0$ with plasticizer concentration for different strain rates.

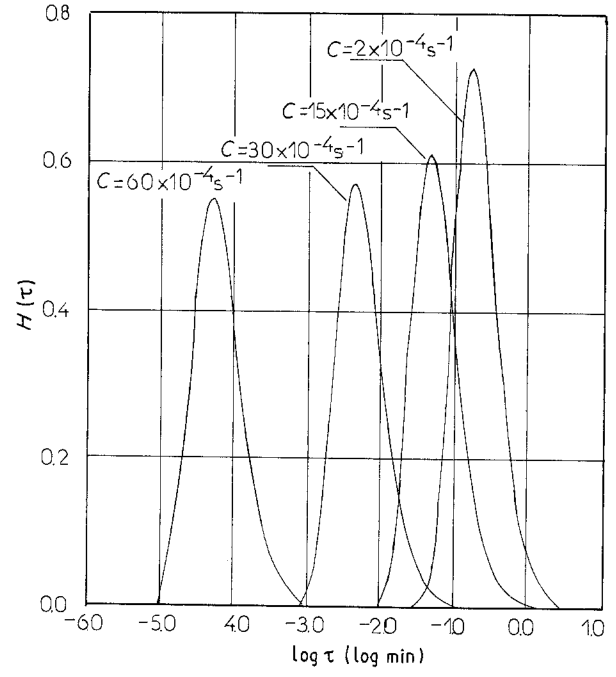

*Figure 9* Curves of the spectral function of $H$ versus $\log \tau_0$ for various strain rates and for a given plasticizer content, $v_p = 0.40$.

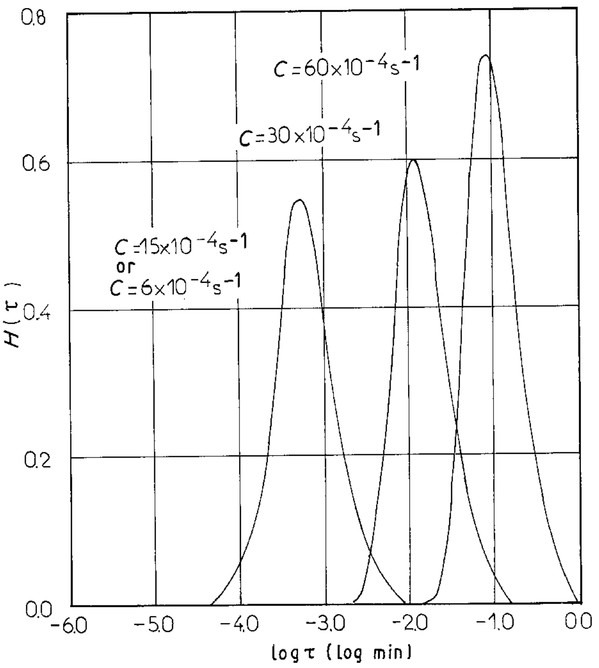

*Figure 10* Curves of the spectral function of $H$ versus $\log \tau_0$ for various strain rates and for a given plasticizer content, $v_p = 0.45$.

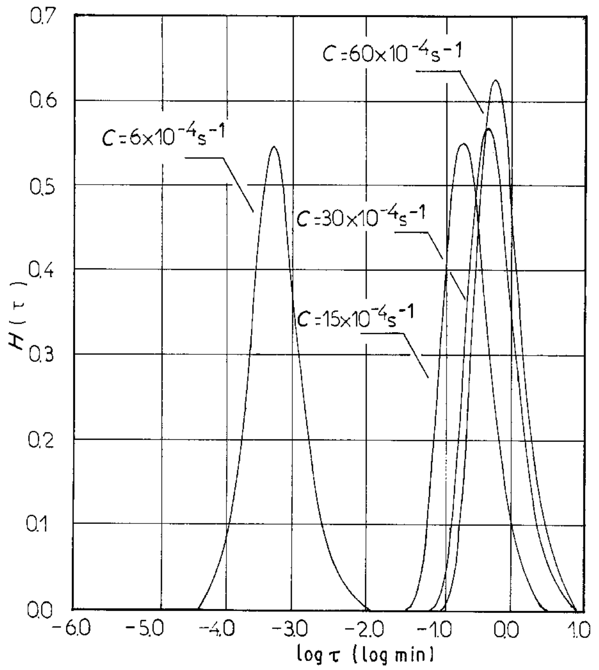

*Figure 12* Curves of the spectral function of $H$ versus $\log \tau_0$ for various strain rates and for a given plasticizer content, $v_p = 0.75$.

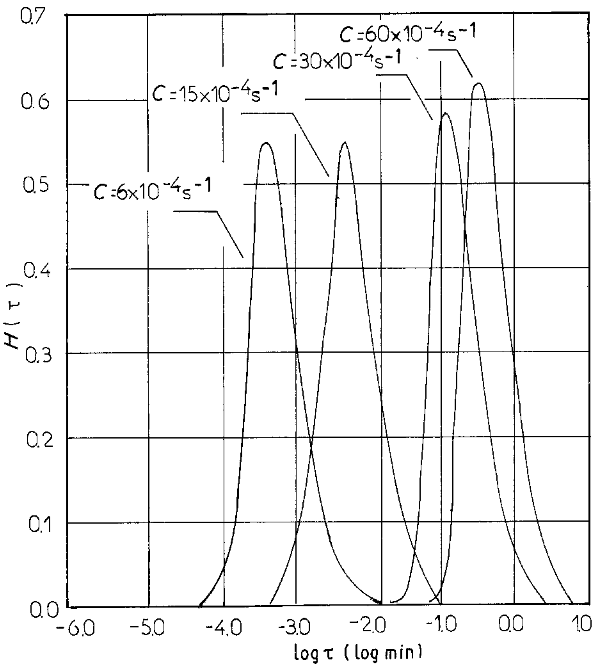

*Figure 11* Curves of the spectral function of $H$ versus $\log \tau_0$ for various strain rates and for a given plasticizer content, $v_p = 0.57$.

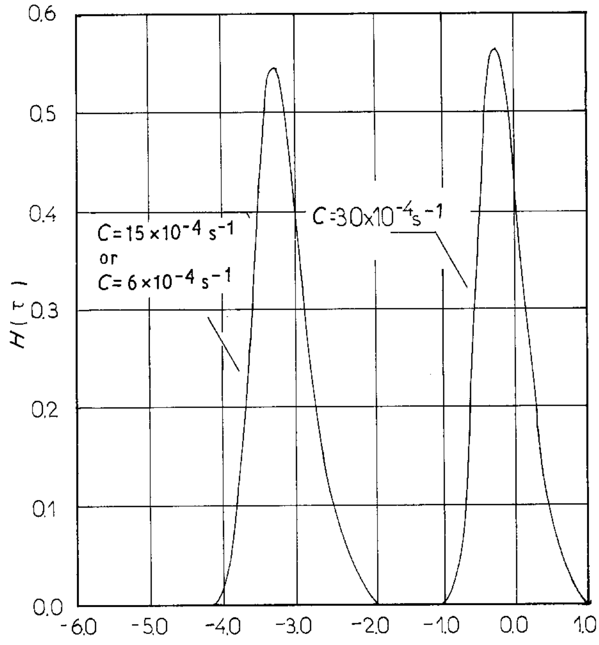

*Figure 13* Curves of the spectral function of $H$ versus $\log \tau_0$ for various strain rates and for a given plasticizer content, $v_p = 0.77$.

constants such as the elastic modulus and the relaxation time. These constants are determined in such a way as to give the closest fit between theoretical predictions and experimental results. However, it is not possible to fit all the curves using only a single relaxation time. Thus, a generalized model containing a spectrum of relaxation times would be more appropriate.

Values of the parameter $\tau_0$ obtained by a computer procedure, as described previously, were plotted in a $\log \tau_0$–$v_p$ diagram as shown in Fig. 8. It may be seen that $\tau_0$ is considerably affected by the plasticizer content only for intermediate strain rates while for both low and high strain rates, $\tau_0$ remain almost constant.

The addition of plasticizer has a noticeable and complex effect on the position of the relaxation time spectra. This is mainly due to polymer network alterations observed in the presence of the plasticizer. Similar phenomena were observed in the case of particulate polymer composites where a change of deformation conditions in the presence of the filler particles, shifts the spectrum to the left, while the effect of filler surface on the properties and structure of the polymer matrix, shifts it to the right [13]. Also, in the same

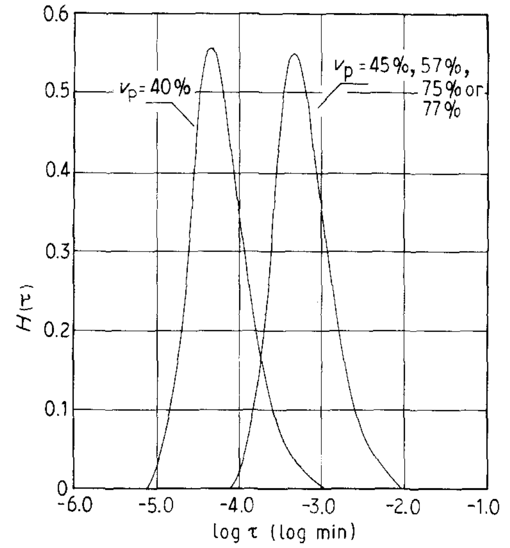

*Figure 14* Curves of the spectral function of $H$ versus $\log \tau_0$ for different plasticizer content and for a given strain-rate, $C = 6 \times 10^{-4} \mathrm{s}^{-1}$.

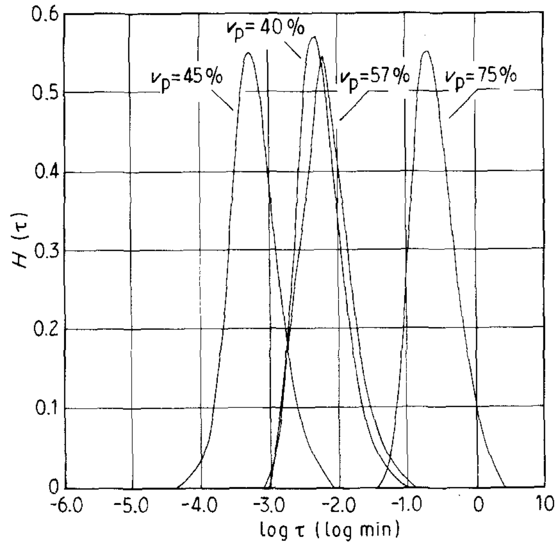

*Figure 15* Curves of the spectral function of $H$ versus $\log \tau_0$ for different plasticizer content and for a given strain-rate, $C = 15 \times 10^{-4} \mathrm{s}^{-1}$.

systems, the findings show an increase of the average relaxation time in the layer of the polymer which is on the surface of solid particles [14, 15].

Fig. 9 illustrates curves of the spectral function of $H$ versus $\log \tau$ for various strain rates and for a given plasticizer content, $v_{\mathrm{p}} = 0.40$. An increase in strain rate, in addition to an expansion of the spectrum, shifts it to the left. Also, the peak value of the spectral function, $H$, increases with decreasing strain rate. The same phenomenon was observed for higher plasticizer concentrations (Figs 10–13).

Fig. 14 illustrates curves of the spectral function of $H$ versus $\log \tau$ for various plasticizer concentrations and for a given strain rate, $C = 6 \times 10^{-4} \mathrm{s}^{-1}$. It is seen that for values of $v_{\mathrm{p}}$ higher than 0.45 the spectra coincide, while for $v_{\mathrm{p}} = 0.40$ the respective spectrum is shifted to the left. However, for higher strain rate, $C = 15 \times 10^{-4} \mathrm{s}^{-1}$ (Figs 15–17) the respective spectra do not coincide and an increase in the plasticizer content shifts the respective spectra to the right.

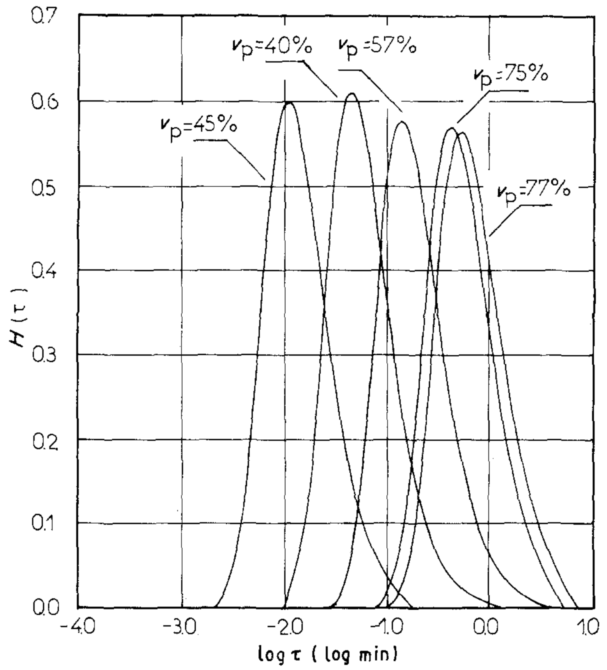

*Figure 16* Curves of the spectral function of $H$ versus $\log \tau_0$ for different plasticizer content and for a given strain rate, $C = 30 \times 10^{-4} \mathrm{s}^{-1}$.

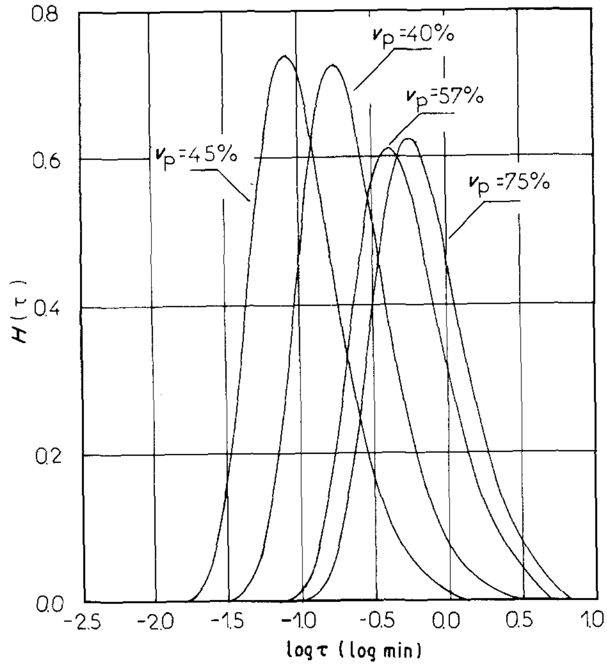

*Figure 17* Curves of the spectral function of $H$ versus $\log \tau_0$ for different plasticizer content and for a given strain rate, $C = 60 \times 10^{-4} \mathrm{s}^{-1}$.

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