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Quantitative Thermomechanical Analysis of Polyvinylchloride Compounds

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Unplasticized, plasticized PVC-compounds and PVC-plasticizer-ethylene vinylacetate copolymer blends were studied by a new differential thermomechanical technique measuring thermally stimulated and isothermal creep, recovery or stress relaxation simultaneously with an unloaded reference sample. The possibilities of quantitative interpretation of such differential thermomechanical curves inside and outside the physical ageing temperature-range is discussed. By the differential technique creep was separated from thermal dilatation and recovery; by a pulsed-load technique recoverable creep was separated from irreversible flow. By these methods plasticized PVC-compounds were found to exhibit multiple glass transition which could not be detected by the conventional techniques, such as differential scanning calorimetry, dynamic mechanical analysis or nuclear magnetic resonance.

By using the Kohlrausch reponse function and the effective (reduced) time method, thermomechanical »temperature-domain« curves could be transformed into the time-domain ones which, in turn, could be transformed into frequency-domain spectra. In order to do this, besides thermomechanical curves, some isotherms were also needed. In the physical ageing temperature-range thermal stimulation was overwhelmed by the effect of the storage- and elapsed time, which would shift the distribution to longer times. In this range the pulsed-load technique with stepwise temperature control was found useful by considering that temperature steps would erase previous history-effects, partly or totally.

The differential techniques was also used to study multiple glass-transitions in blends of PVC di-iso-octyl phthalate and ethylene vinylacetate copolymer.

INTRODUCTION

The thermomechanical technique was introduced quite long ago by Kargin and Slonimsky[1]. At first it involved measurement penetration of a spherically tipped indentor into the specimen by continuously increasing temperature. In this way several transitions could be detected which were attributed to changes of structure and/or of molecular mobility in polymers. These transitions could be correlated with those measured by dynamic mechanical analysis (DMA), dielectric spectroscopy, differential scanning calorimetry (DSC) and broad or spin-echo nuclear magnetic resonance (NMR).

The method, however, was found to be too qualitative. Much later, by the development of the experimental technique and by the easy accessibility of microcomputers the problem has re-gained interest[2]. By a microprocessor controlled instrument built in the author's laboratory it has become possible to measure thermomechanical curves in extension, compression and torsional modes in creep, recovery and stress relaxation regimes and also the microprocessor enabled quantitative interpretation of such curves. A part of the technique is referred to as »thermally stimulated« creep, — recovery and — stress relaxation and may be compared to the well known thermally stimulated dielectric polarization and depolarization measurements. For a review of the combination of various methods for detecting transitions see Hedvig[3].

The aim of this work is to introduce new techniques for the measurement and methods for quantitative interpretation of thermomechanical curves of polyvinylchloride compounds and for their transformation into isotherms, even in the glassy state where physical ageing is effective. This problem is essential in the long term prognosis of mechanical properties and also in studying phase transitions.

THEORETICAL CONSIDERATIONS

The response of a material to external mechanical actions is described by non-equilibrium thermodynamics. For an introductory review see Baur[4] and the literature cited therein. Phenomenological viscoelastic theory is also based on the principles of non equilibrium thermodynamics. In the phenomenological theory based in the Gibbs formalism relations between intensive variables — such as temperature, pressure (load), chemical potential — and intensive ones — such as free energy, enthalpy, entropy, volume, are established without considering the microstructure. In the more elaborate theories these relations are derived from some properties of the microstructure by using the classical — or quantum-statistical theory. See e. g. Zoubarov[5].

Independently of the kind of approach, an important basic conclusion is that by knowing the response of the system to an infinitesimally rapid action (delta-function or stepfunction) it is possible to calculate the response to any time dependent stimuli. At the first (linear) approximation, if the response (deformation, ε) to a step-function external load (stress, σ) is $\Phi_c(t)$, the deformation caused by any temperature dependent load, $\sigma(t)$, is expressed as

$$\varepsilon(t) = J(o)\,\sigma(t) + [J(\infty) - J(o)] \int_{t'=o}^{t} \frac{d\,\Phi_c(t'-t)}{dt'}\,\sigma(t')\,dt' \tag{1}$$

where $J(o)$ and $J(\infty)$ are the limiting (»unrelaxed« resp. »relaxed«) compliances. Function Φ_c in this representation is dimensionless and is normalized to have values in-between zero and unity. »Linearity« means here that the response is independent of previous actions and the response function is independent of the stress.

The nonlinear cases can also be handled but the expressions are more complex; in Equ. (1) σ cannot be separated from the response function Φ_c.

By sinusoidal loading Equ. (1) represents a Fourier transformation resulting in frequency-dependent real (storage) and imaginary (loss) deformation i. e. compliance-components.

An isothermal creep measurement is equivalent to measuring the creep response function, provided that the load is applied very quickly and the duration of the measurement is long. This will be referred to as a time domain experiment. Measurement of the storage- and loss-compliances as a function of the frequency is referred to as a frequency-domain experiment.

The creep compliance, $J(t) = \varepsilon(t)/\sigma_o$, exhibits a recoverable »elastic« and an unrecoverable »plastic« component. σ_o is here the constant stress. Also in many practical cases there are frozen-in stresses in the sample originating from its processing. These stresses would induce deformation (recovery) which is added to that caused by the external load.

In principle, such frozen-in stresses may be eliminated by annealing but, in many cases, this procedure would change their morphological structure, which, of course, has to be avoided.

Considering this and also the temperature dependence on the quantities, the creep compliance is expressed as

$$J(t, T) = J(o, T) + [J(\infty, T) - J(o, T)]\, \Phi_c(t, T) + J_R\, \Phi_R(t, T) + \frac{t}{\eta(T)} \tag{2}$$

where Φ_c is the dimensionless creep response function normalized as $\Phi_c(o) = 0$, $\Phi_c(\infty) = 1$; Φ_R is the recovery-function of the frozen-in deformation normalized $\Phi_R(o) = 1$, $\Phi_R(\infty) = 0$, J_R being the total frozen-in value in compliance units; η is the viscosity of irreversible flow. The limiting compliances at zero, $J(o, T)$, and infinite times, $J(\infty, T)$, are also generally temperature dependent.

For convenience, the last term of Equ. 2, describing non recoverable viscous flow, can also be expressed in terms of a function $\Phi_v(t, T)$ with an amplitude J_v of compliance dimension. J_v will be referred to as the plastic (viscous) part of the compliance.

The total creep compliance is, thus, expressed as

$$J(t, T) = J(o, T) + [J(\infty, T) - J(o, T)]\, \Phi_c(t, T) + J_R\, \Phi_R(t, T) + J_v\, \Phi_v(t, T) \tag{3}$$

In general, stress and strain and, consequently, the compliances too are tensors but this is not considered here since it does not affect the discussion which follows.

In order to be able to transform one isothermal creep curve into another, each term of Equ. 3 should be transformed. Φ_c may be transformed by »horizontal« shift provided that its shape is unchanged by changing the temperature. This requirement is often fulfilled when the new temperature falls within the range of a transition.

Stress Relaxation and Recovery

Similarly to Equ. (1), the stress-response to a strain-function $\varepsilon(t)$ is expressed as

$$\sigma(t) = E(o)\, \varepsilon(t) + [E(o) - E(\infty)] \int_{t'=o}^{t} \frac{d\, \Phi_\sigma(t - t')}{dt'}\, \varepsilon(t')\, dt' \tag{4}$$

where $E(o)$ and $E(\infty)$ are the limiting moduli, Φ_σ is the stress relaxation response function normalized as $\Phi_\sigma(0) = 1$, $\Phi_\sigma(\infty) = 0$.

At constant strain (step-function) the stress relaxation modul is

$$E(t) = E(\infty) + [E(0) - E(\infty)]\,\Phi_\sigma(t) \tag{5}$$

It is easy to show from Equ. (4) that the Young modulus determined from a stress-strain curve as its slope, $d\sigma/d\varepsilon$ is equal to the stress relaxation modulus expressed by Equ. (5) at a fixed load time t.

Within the limits of linearity the inter-relations between the creep compliance $J(t) = \varepsilon(t)/\sigma_0$ and stress relaxation modulus $E(t) = \sigma(t)/\varepsilon_0$ are

$$\int_{t'=0}^{t} E(t')\,J(t-t')\,dt' = t \tag{6}$$

$$\int_{t'=0}^{t} J(t')\,E(t-t')\,dt' = t$$

These integrals can be calculated numerically by the method of Hopkins and Hamming[6].

Recovery may be measured after creep or after stress relaxation either by interrupting the process or by waiting for the new equilibrium under constant stress or strain. In ideal elastomers there is no stress relaxation and recovery is complete. In visco-elastic materials recovery is retarded by the mechanical loss and may not be complete. The unrecovered part is due to the viscous flow involving mass-transport or change of structure and is to be sharply distinguished from the mechanical loss arising from dissipation of heat during a recoverable relaxation process.

In the following discussion, for convenience, recoverable creep and stress relaxation will be referred to as relaxation processes, keeping in mind the difference between these two phenomena. Conventionally, the characteristic times governing creep are referred to as retardation times, those governing stress relaxation as relaxation times.

Response Functions

For analytical description of the creep-, recovery-, and stress relaxation -response functions the phenomenological approach of non-equilibrium thermodynamics is not successful; one has to know something about the microstructure of the material. The usual approach is to start from the assumption that the interaction among the microscopic units of the material is negligible with respect to the thermal energy. In such cases the response function is simply exponential, e. g. for stress relaxation $\Phi = \exp(-t/\tau)$, where τ is referred to as relaxation time. For interacting particles the weighted sums of exponentials are used for approximating the response function (relaxation time distribution concept). Phenomenological thermodynamics considering the existence of many internal degrees of freedom, but not considering interaction (coupling) among them, results in similar exponential response functions[4].

In solid polymers the interaction among »units«, which any thermodynamical treatment is based on is evidently very strong. Moreover, these units, which should behave »rigidly« by thermal motion, are different in different temperature ranges. In order to define them the chemical and physical structure of the material is to be known. It is evident, anyway, that some of these units are parts of the polymer molecule i. e. they are connected with chemical bonds. The intermolecular forces are also strong in comparison to thermal energy, so the application of the relaxation time distribution concept in solids is not successful. Attempts to describe creep, recovery and stress relaxation response functions in this way result in expressions having at least 10—12 parameters to which not much physical meaning can be attributed. On the other hand, long-term experiments show that the response functions can be fairly well described by 2- or 3-parameter-functions. Quite a number of such functions have been proposed on the basis of some general properties of the solid. The most widely used one is that introduced in the last century by Kohlrausch[7]

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{N}\right] \tag{7}$$

where τ is a relaxation time dependent parameter, exponent N is in-between 0 and 1 and is only slightly dependent on temperature.

The wide practical applicability of the Kohlrausch response function made us prefer it to others as e. g. those introduced by Gény and Monnerie[8] and Jonscher[9], although these are based on realistic physical models while no such model has been found for the Kohlrausch function yet. We tried to use various functions to describe mechanical and dielectric responses but no better fitting was found in any case than that obtained by the Kohlrausch function.

Figure 1. shows a typical set of Kohlrausch stress relaxation curves according to Equ (7) at $\ln \tau = 10$ by changing the exponent N in steps. Creep curves can be constructed by using Equations (6) but in practice the creep process can be sufficiently well described by using the complementary Kohlrausch function $\Phi_k = 1 - \Phi_k$.

Figure 2 shows the corresponding storage- and loss-moduli obtained by Fourier transformation of some of the response curves of Figure 1 illustrating a transition displayed in the frequency domain. The Fourier transforms of the Kohlrausch function cannot be expressed in analytical forms.

Another, very widely used representation is to plot the response to sinusoidal load at a single frequency as a function of the temperature. This is usually termed as dynamic mechanical analysis (DMA) and is essentially a thermomechanical method. DMA-spectra can also be described by the Kohlrausch function by introducing the temperature dependence of parameters τ and N.

Shift-methods. Effective Times

In many cases by changing an extensive variable such as temperature, pressure, or even in nonlinear cases the stress, would shift the response

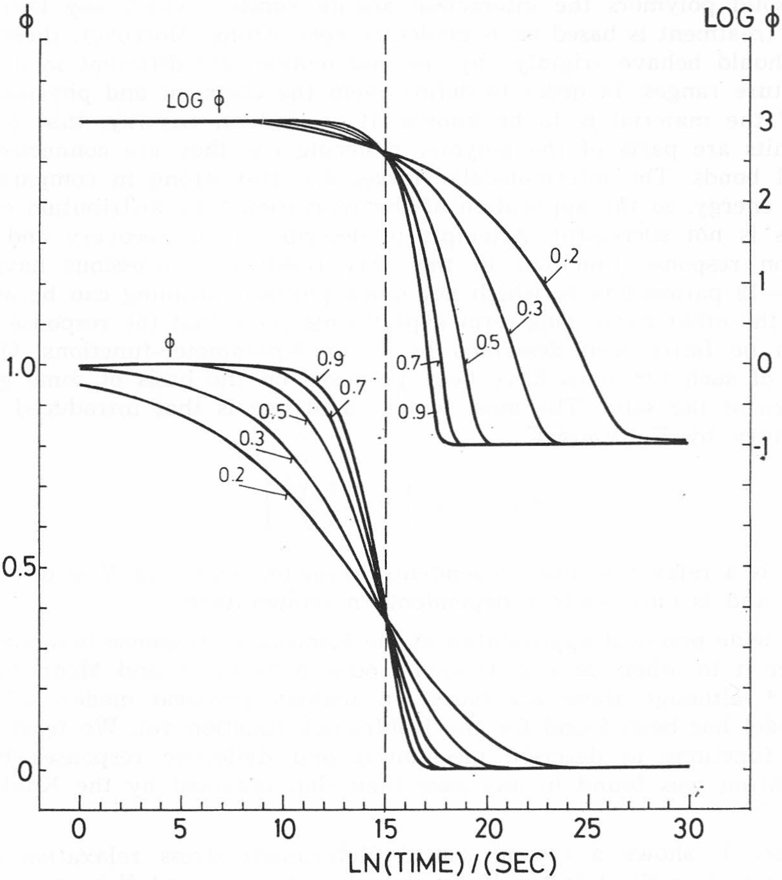

Figure 1. The Kohlrausch response function $\Phi(t) = \exp\{-(t/\tau)^N\}$ at $\ln \tau = 10$ and different N-values.

function in the time scale without changing its shape. Shift factors caused by such a variable Y may exhibit Arrhenius dependence

$$a_Y(Y, Y_r) = \exp \frac{E}{R} \left\{ \left(\frac{1}{Y} - \frac{1}{Y_r} \right) \right\} \tag{8}$$

or Williams-Landel-Ferry (WLF) dependence (see e. g. in Ref. 3).

$$a_Y(Y, Y_r) = \exp \left\{ \frac{A(Y - Y_r)}{B + Y - Y_r} \right\} \tag{9}$$

where index r refers to the reference state.

By interpretation of thermomechanical curves the variable is $Y = T$ (temperature), which is time-dependent.

In most amorphous and semicrystalline polymers above their glass transition temperature the WLF equation (9) is useful for describing temperature-

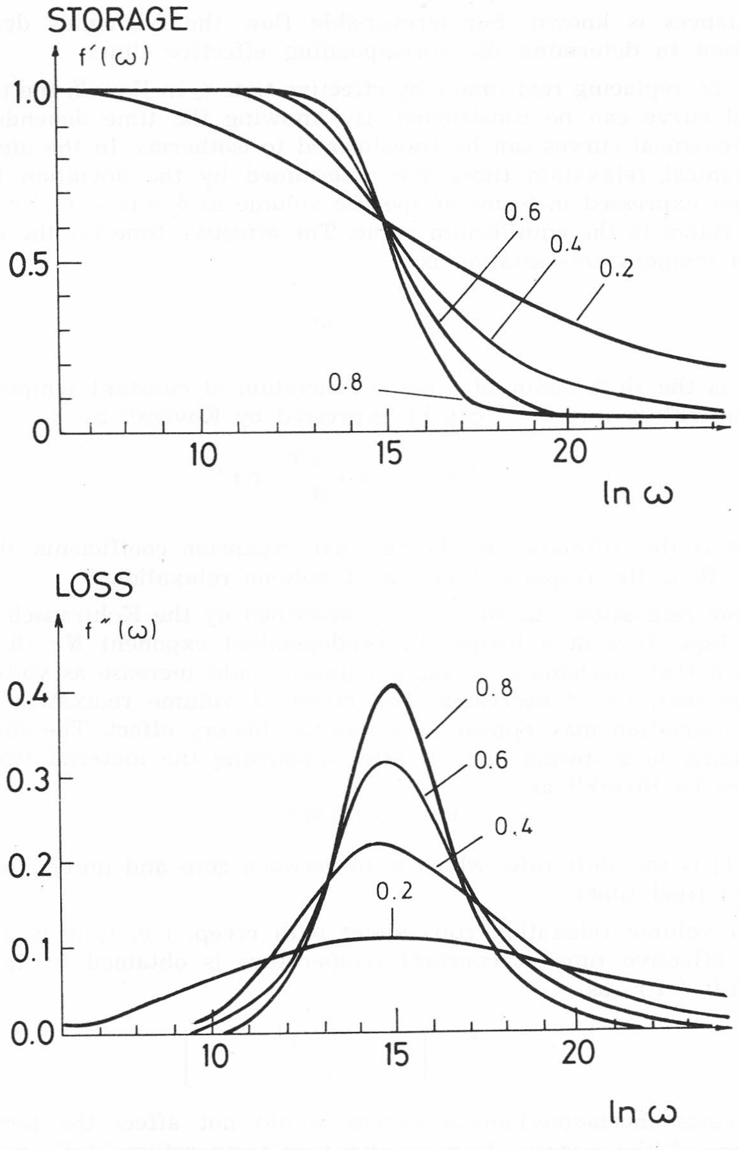

Figure 2. Fourier transforms of the Kohlrausch response function of Figure 1. $f'(\omega)$: real part: $f''(\omega)$ imaginary part.

-shifts of isothermal creep and stress relaxation curves. By introducing effective (reduced) times

$$t_e = \int_{t'=0}^{t} a_T^{-1}\,[T(t'), T_r]\,dt' \tag{10}$$

instead of real times, the thermomechanical curves can be transformed to isotherms provided that the temperature dependence on the limiting moduli or compliances is known. For irreversible flow the Arrhenius dependence can be used to determine the corresponding effective time.

Thus, by replacing real time t by effective time t_e in Equ. 3, the thermally stimulated curve can be constructed. By knowing the time dependence, the thermomechanical curves can be transformed to isotherms. In the glassy state the mechanical relaxation times are determined by the deviation from the equilibrium expressed in terms of specific volume as $\delta = (v - v_\infty)/v_\infty$, where index ∞ refers to the equilibrium value. The effective time for the combined time- and temperature-variation is

$$t_e = \int_{t'=0}^{t} a_T^{-1} a_\delta \, dt \tag{11}$$

where a_δ is the shift factor of volume relaxation at constant temperature T. The dimensionless variable δ can be expressed by Kovacs[10] as

$$\delta(t_e) = -\triangle a \int_0^{t_e} \Phi_\delta (t_e - t_e') \frac{dT}{dt_e'} \, dt_e' \tag{12}$$

where Δa is the difference of the thermal expansion coefficients above and below T_g, Φ_δ is the response function of volume relaxation.

Volume relaxation was successfully described by the Kohlrausch response function (Equ. 7) with a temperature-independent exponent $N \approx 0.5$.[10] Also, it is known that mechanical relaxation times would increase as volume relaxation proceeds, i. e. δ decreases. The effect of volume relaxation to creep or stress relaxation may appear as a thermal history effect. The shift factor corresponding to a storage time t_s after quenching the material from above T_g is given by Struik[11] as

$$\ln a_\delta = c(T) \ln t_s \tag{13}$$

where $c(T)$ is the shift rate, which is in-between zero and unity; the storage time $t_s \gg t$ (real time).

When volume relaxation runs along with creep, i. e. t_s is in the order of t, the effective time at constant temperature is obtained by integration of $a_\delta = (t_s/t + t_s)^c$ as

$$t_e = \frac{t_s}{1 - c} \left[\left(1 + \frac{t}{t_s} \right)^{1-c} - 1 \right] \tag{14}$$

In such cases thermomechanical curves would not affect the temperature dependence of the process because the time-temperature shift, which acts opposite to volume relaxation-shift, only slightly depends on temperature below T_g, in contrast to that above T_g.

Another complication is that, during a thermomechanical measurement, the effect of the initial storage time may be partly or completely erased by heating. This effect can be calculated on the basis of Equ. (12). Mechanical response in the glassy state was proven to be determined uniquely by the specific volume, i. e. parameter δ, no matter which way it had been reached[11].

The important conclusion is that in the glassy state the increase of temperature does not necessarily increase creep- or stress relaxation-rate (decrease relaxation times); the overall effect mainly depends on the thermal history.

EXPERIMENTAL

Isothermal creep and stress relaxation can be measured only in a limited time scale. Even a single transition may cover 4—5 decades of time. In order to detect several transitions measurement in a very wide range would be necessary, starting from microseconds to years. Recently, very fast electronics, down to the nanosecond range, have become widely available, so time-domain mechanical spectroscopy starts to offer new possibilities. In the frequency domain very wide frequency range may be covered but this rather complicated instrumentation, involving difficulties in the measurement of absolute values of compliances or moduli in different frequency ranges.

These technical difficulties made the experimentators choose the temperature domain technique, especially by using sinusoidal periodic stresses or strains (DMA). For a fair quantitative information of DMA-curves, i. e. »mechanical spectra«, the experiment should be repeated at different frequencies, preferably in a wide frequency range.

The usual DMA devices, however, can be used only in a narrow frequency range, which is not enough for determination of the WLF-constants (or activation energy) of the transitions. By combination of various relaxation methods for typical polymers, transition maps have been constructed (See in Mc Grum et al.[12], Hedvig[13]).

Although the agreement between the transition constants obtained by various methods (mechanical, dielectric, nuclear magnetic, electron spin a.s.o.) is fair, the absolute values of the transition frequencies and the response functions are often different. Also, because of the limitations of the shift methods, the information contained in a set of DMA curves measured at different frequencies is not sufficient for obtaining enough information about the transition, and certainly not enough for determining the response function.

So, the temperature domain DMA is proved to be very useful for studying transitions — similarly to optical, dielectric and magnetic spectroscopies — but certainly not for quantitative description of creep and stress relaxation processes. Moreover, DMA is unable to separate creep from viscous flow and from the recovery of frozen-in deformation.

Thus, it seems more useful to turn back to the straigthforward method of measuring a series of isotherms, using the up-to-date fast-response transducers and digital electronic data-processing facilities in order to obtain the parameters of the transitions.

Automated Measurement of Isotherms

Within the range of linearity, sets of isotherms for the construction of creep master curves and for determination of storage- and loss-compliances can be measured by a temperature program shown in Figure 3 for recording consecutive creep — and recovery — processes. By this scheme, creep is measured under isothermal conditions by stepwisely changed temperature, while recovery is observed in-between the load-periods when temperature is raised. In the creep period, the deformation may be sampled so that numerical Fourier transformation is made easy. Thus, if required, storage (J') — and loss (J'') — compliances at different temperatures may also be calculated. For such a transformation, with an accurracy of $\pm 0.1\%$, the following formulae were used after Struik and Schwarzl[14]

$$J'(\omega_o) = 1.46789\, J(1.06\, t_o) - 0.8713\, J(4.37\, t_o) + 0.3912\, J(5.76\, t_o)$$

$$J''(\omega_o) = 0.47\,[J(4t_o) - J(2\,t_o)] + 1.715\,[J(2t_o) - J(t_o)] + \qquad (15)$$

$$+ 0.902\,[J(t_o/2) - J(t_o/4)]$$

$$\omega_o = 1/t_o$$

where t_o is a pre-set time from loading, ω_o is the corresponding angular frequency.

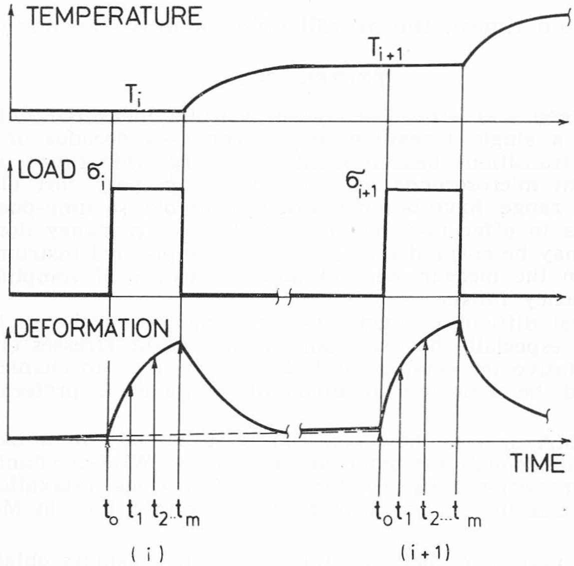

Figure 3. Temperature, load and sampling program for the pulsed load thermo-mechanical measurement (see text).

From Equs (15) it is seen that for such a transformation 8 compliance-values are needed. By changing t_o, the corresponding ω_o can also be changed. The frequency-range covered is, thus, limited by the fastness of the transducer- and sampler-system on the high frequency side, and by the duration of the experiment on the low frequency one. Besides, the storage and loss compliances of the linear viscosity describing irreversible flow can also be obtained from this experiment.

As discussed in the previous chapter, such a transformation from time — to the frequency — domain is not at all necessary. What is really needed is the response function and also the parameters of the transition, especially the shift factors. These are obtained most directly from a series of isotherms. The master curve is obtained from this set by fitting to the Kohlrausch response function of Equ. (7) substracting the unrecovered (plastic) part of the compliance (last term of Equ 3), which is directly measured by the pulsed creep-recovery method shown schematically in Figure 3. Instead of simple graphical shifting parameter τ (or rather $\ln \tau$) is added to that of the reference till the best fit is obtained. In this procedure the other parameters (limiting-values, exponent) are also taken into account.

Differential Technique

In order to obtain a fair accuracy in determining the parameters of the response function, the effects of frozen-in stresses and those of thermal dilatation have to be corrected for. This is simply done by using a differential technique, i. e. using a reference sample cut from the solid polymer along the streamline of its orientation. The deformation of the loaded sample is substracted from that of the unloaded, reference, one; thus, the recovery of frozen-in deformation and thermal dilatation are eliminated.

If $\triangle l_{si}$ and $\triangle l_{ri}$ are the changes of length of the sample and reference, respectively, and F_{oi} is the constant load (force), the elastic part of the compliance in the i-th load pulse is determined as

$$J_i^{(e)}(t) = \frac{A}{F_{io}} [1 + \varepsilon_i(t)]^{-1} \ln [1 + \varepsilon_i(t)] \tag{16}$$

where A is the cross-sectional area of the sample and

Recovery. Time- and Thermal-Sampling

Measurement of the release of frozen-in deformation offers a very efficient way for studying transitions. In solid polymers transitions often consist of multiple relaxation processes, which are difficult to separate from DMA, DSC, thermomechanical — creep or — stress relaxation curves. Another possibility of detecting transitions is to strain the specimen above or within the transition temperature-range, cool it down in the strained state and then, by removing the strain, heat it up linearly and watch the deformation as a function of the temperature. Such an experiment can be performed in different ways; some of them are shown in Figure 4.

One way is to use constant strain or stress at a temperature T_L and inmediately cool down the sample at a constant rate. Then, after removing the load, heat it up at the same rate and measure the recovery of deformation (Figure 4a).

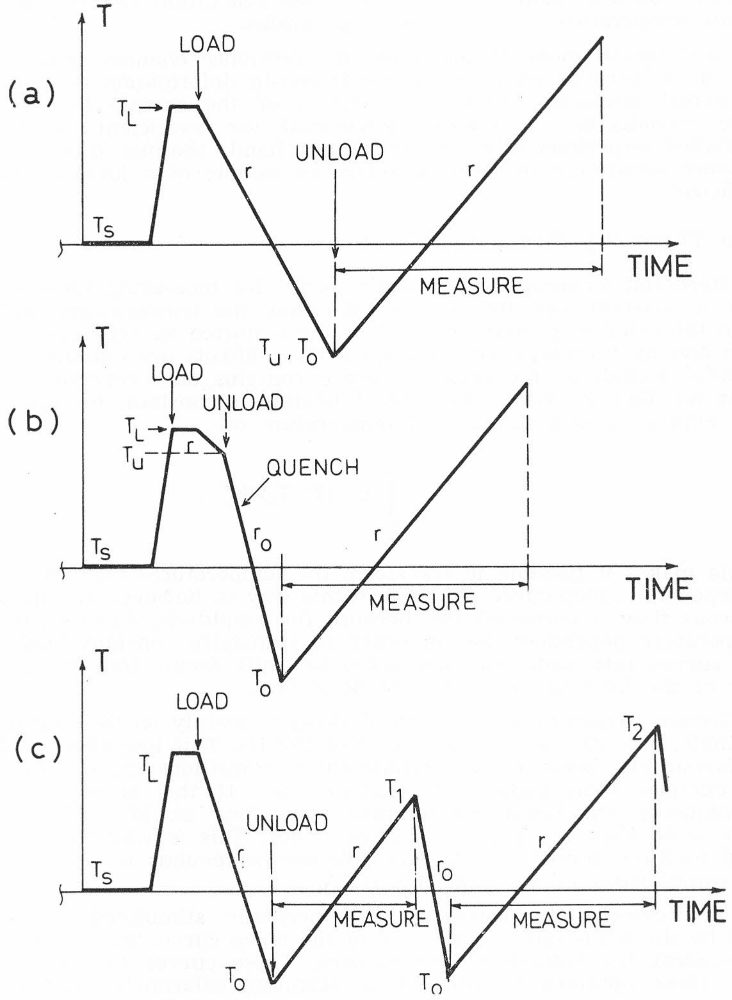

Figure 4. Sove ways of conducting thermally stimulated recovery experiments (see text).

$$\varepsilon_i = \frac{\triangle l_{si}}{l_{osi}} - \frac{\triangle l_{ri}}{l_{ori}} \tag{17}$$

l_{ori} and l_{osi} being the sample lengths before the i-th load-pulse. The unrecovered, »plastic« part of the compliance is calculated as

$$J_i^{(p)}(t) = \frac{A}{F_{oi}}[\varepsilon_{i+1}(o) - \varepsilon_i(o)] \tag{18}$$

where $\varepsilon_{i+1}(o)$, $\varepsilon_i(o)$ are the differential engineering strains according to Equ. (17) just before the application of load pulses $i + 1$ and i, respectively (see Figure 3).

With the device built in the author's laboratory, four samples can be measured simultaneously in extension or compression modes. 1 or 2 samples may be used as reference. The device is microprocessor-controlled and is equipped with an automatic force control facility. Creep and stress relaxation can be measured by using various temperature — and load — programs.

In the differential mode of operation, the reference channel shows thermally stimulated (or isothermal) recovery of the frozen-in deformation or, for annealed samples, thermal dilatation. Thermal dilatation of the sample holder-system is corrected by introducing a 5th order polynomial, the coefficients of which have been determined experimentally. On the other hand, thermal dilatation can be measured more accurately by using a reference sample of a known (small) dilatation coefficient.

Differential Thermally Stimulated Creep

The differential technique is especially useful for measuring thermally stimulated creep at constant load by linearly increasing the temperature. Such curves, measured in the usual way, may be considerably distorted by recovery of frozen-in deformation and by thermal dilatation. Since these effects are eliminated by using the differential technique, the resulting curve contains only reversible creep and viscous flow (cf. Equ. 3). When the rate of heating is constant, the effective time of creep is expressed as a function of temperature as

$$t_e(T) = \frac{1}{T}\int \alpha_T^{-1}(T', T_o)\,dT' \tag{19}$$

This formula makes it possible to transform the temperature-scale into time-scale. The time-dependent creep curve obtained in this way is, however, not quite correct, even if viscous flow is corrected for, because the amplitude, $J(\infty) - J(o)$, in Equ. (3), is temperature dependent. So. in order to transform constant load thermally stimulated curves into isotherms not only the shift factor but the temperature dependence of the limiting values has to be known.

The effective frequency of this method depends mainly on the rate of heating; correspondingly, it is very low: in the order of 10^{-4} Hz. This low effective frequency is often favourable because low temperature transitions have usually lower activation energies than higher temperature ones. If this is so, by increasing effective frequency the lower temperature transitions would shift more in the temperature scale than the higher frequency ones. This is why the resolution in determining multiple transitions in solid polymer compounds is usually higher by thermally stimulated methods than by DMA.

Transitions detected by constant load thermally stimulated creep may be represented by the temperature derivative of the creep curve, the maxima of which roughly represent the transition temperatures. These curves can be easily compared with those obtained by differential scanning calorimetry (DSC), DMA or spin-echo NMR, (see e. g. in ref.[3]). From a single thermally stimulated creep or stress relaxation curve, however, the isotherms cannot be constructed without additional studies.

This experiment can be repeated at different load-temperatures T_L in order to freeze different parts of the distribution. When the sample is unloaded before reaching the initial temperature T_o of the recovery measurement, as shown in Figure 4b, a part of the distribution is frozen-in. After unloading, the sample is quenched at a rate $r_o \gg r$. The range $T_L - T_u$ is referred to as a »temperature window«. By changing T_L and the width of the window the distribution can be traced in narrow parts.

It is also possible to perform thermally stimulated experiments partially, as shown in Figure 4c. After loading and cooling down to temperature T_o, recovery is measured up to a temperature T_1, and only then it is quenched to T_o again. In the first cycle, a part of the distribution is recovered; subsequent heating should therefore detect the remaining part only. This method proved to be efficient for discovering inhomogeneously broadened transitions.

Another, not yet exhausted, possibility is to perform thermally stimulated recovery measurements after quenching the sample at different stages of creep or stress-relaxation. In the stress relaxation mode, the frozen-in deformation is kept constant; so, by quenching different stages of the relaxation process may be frozen-in and subsequently released. This method may be termed »time-sampling«.

Differential Thermally Stimulated Stress Relaxation

By measuring thermally stimulated stress relaxation, the sample is strained up to a certain level and the stress is measured while the temperature is raised linearly. By interpretation of such thermomechanical curves, effects of the recovery of frozen-in deformation and thermal dilatation are to be considered similarly to creep. Thermal dilatation would make the relaxing stress smaller, while recovery of frozen-in deformation may make it larger or smaller depending on the orientation of the sample.

By using the differential technique, these effects are, at least partially, corrected for. The unstrained reference samples show the temperature dependence of the strain; so, the modulus is expressed as

$$E(T) = \frac{F(T)}{\triangle} \left[\frac{\triangle l_s - \triangle l_r(T)}{l_o} \right]^{-1} \tag{20}$$

where F is the force, which is directly recorded, A is the cross-sectional area of the sample, $\triangle l_s$ and $\triangle l_r$ are, respectively, the deformations of the sample and reference, l_o is the (equal) length of the sample and reference at the starting temperature. The experiment is made so that $\triangle l_s$ does not change with temperature. Evidently, the condition of constant strain cannot be ensured by thermally stimulated stress relaxation because of the dilatation effect but it is so also in creep experiments: at constant load, the stress continuously increases by deformation because the cross-sectional area decreases. This is partially accounted for by using true stress and true strain, as done in Equ. (16) but this strictly holds only if volume is constant, i. e. Poisson's ratio is 0.5. Corrections for such effects at low (1—5%) deformation levels are not necessary.

An interesting new experimental possibility is offered by conducting the stress relaxation experiment by scanning the temperature downward. When thermal dilatation is linear, this is similar to making a stress-strain experiment with constant strain rate at very small strain levels while temperature is decreased. At high temperatures, the measured modulus is close to the relaxed stress relaxation-modulus-limit, $E(\infty)$.

By decreasing the temperature, the modulus increases and reaches the unrelaxed limit $E(o)$ by passing through a transition. Since the strain rate (dilatation) can be simultaneously and independently measured by the differential technique, interpretation of such »inverted« thermomechanical curves is possible.

In highly oriented, stretched, samples the frozen-in strain may be so high that under constant strain considerable shrinkage forces may be generated by heating. Thus, a thermomechanical measurement may be carried out by fixing the dimensions of the sample or by applying a small, constant, strain and measure the force while the temperature is scanned linearly upward. At the temperature range of thermally stimulated recovery, a considerable increase of the force is observed. The differential technique using unstretched reference samples is also helpful in this case, in order to correct for thermal dilatation.

The microprocessor controlled device constructed in the author's laboratory, called »Multirelax«, is capable of making all the isothermal and thermomechanical experiments described above in a fully automated way. Creep, recovery and stress relaxation experiments can be performed in different atmospheres (even in liquids) in a wide temperature range (from —150 °C up to +500 °C). Additionally, a small stress-strain machine was also constructed for operation in a wide temperature range. This machine is also operated by the microprocessor of the Multirelax system.

RESULTS AND DISCUSSION

Using the microprocessor controlled differential thermomechanical technique several polymer compounds have been studied and the results analyzed. Only a few examples on PVC-compounds will be discussed here.

Study of Phase-Transitions by the Thermomechanical Technique

Like conventional DMA, the different thermally stimulated techniques are found very useful for studying phase-transitions in polymer compounds. For qualitative studies the constant load thermally stimulated creep technique may be used in extension, compression or torsion.

The resolution is considerably higher than that of conventional (sinusoidal) DMA because the effective frequency is smaller. As it was discussed in chapter 2, in such simple thermally stimulated curves several mechanisms are superimposed. By the present differential technique thermal dilatation and recovery of frozen-in deformation effects are cancelled out, but irreversible flow is still mixed with creep.

Unplasticized PVC is amorphous, it is known to exhibit two transitions: the glass-rubber transition around 80 °C and a broad secondary (β)-transition centered around —50 °C at 1 Hz. Plasticized PVC exhibits a single, broad, glass transition range depending on the amount and kind of plasticizer. This transition appears homogeneous when studied by DSC, DMA or NMR. By the thermomechanical technique, the multiplicity of the transition is found to indicate phase-heterogeneity of the system. We studied this heterogeneity before, at different stages of processing, by combining thermally stimulated creep with thermally stimulated dielectric depolarization techniques.[15] Figure 5 shows an example of this heterogeneity: a compression-mode constant load differential thermally stimulated creep curve and its derivative is plotted as a function of the temperature. The derivative is found useful for characterizing the transitions; it roughly corresponds to the relaxation time distribution. It is seen that in this conventional plasticized compound at least 3 transition bands can be distinguished corresponding to different phase-structures. Since the higher temperature band is close to the T_g of unplasticized PVC, it is concluded that plasticization is not complete. Such remaining unplasticized parts are always found regardless of how well the sample is processed.

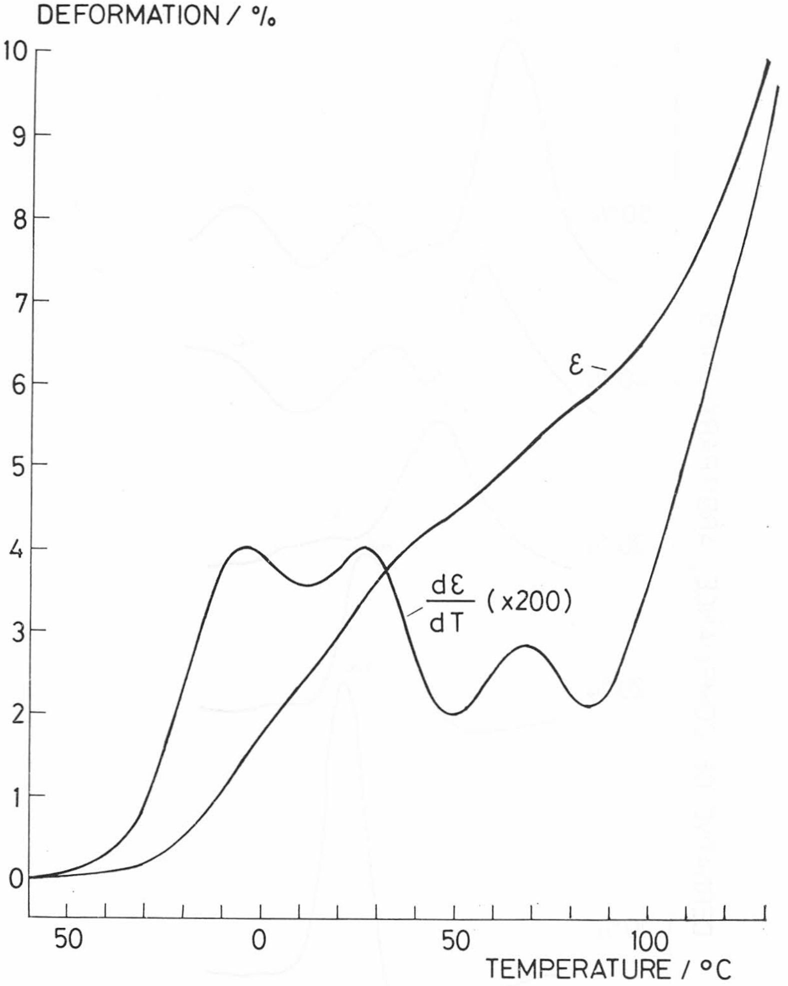

Figure 5. Result of a constant load compressional differential thermally stimulated creep experiment for a typical plasticized PVC compound. Rate of heating 1 °C/min.

Figure 6. shows a series of derivative curves corresponding to compounds containing different amounts of plasticizer (di-iso-octyl phthalate). The peaks of the derivative-curves represent transition bands. It is seen that the main transition, labelled α, is shifted to low temperatures as expected, but by increasing the plasticizer content new bands (α', α'') appear, indicating phase-heterogeneity. Such heterogeneity is found in all kinds of plasticized PVC-compounds.

Figure 7. shows a typical example of a pulsed-load differential thermomechanical analysis of a blend of plasticized polyvinylchloride with ethylene vinylacetate copolymer. This compound exhibits two glass transition temperatures and the blend is phase-heterogeneous. In Figure 7, the elastic part

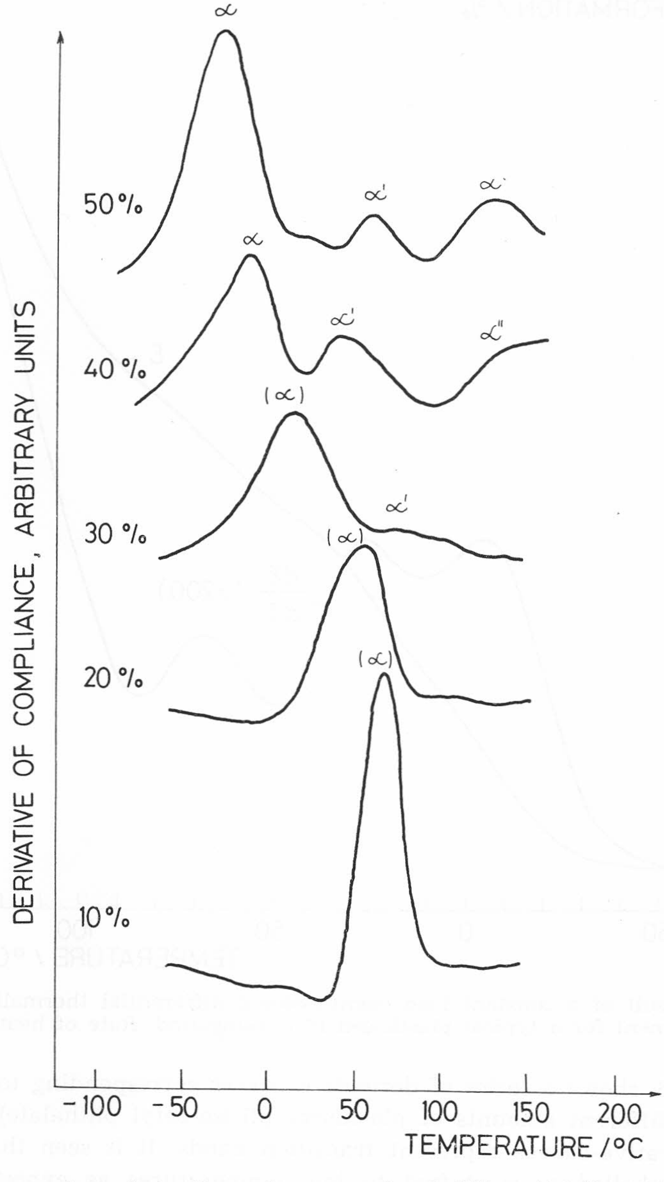

Figure 6. Temperature derivatives of compressional differential thermally stimulated creep curves for a series of plasticized PVC-compounds. The plasticizer (di-iso-octyl phthalate) content is indicated in weight percents.

of the isochronous compliance, its derivative and the irreversible »plastic« part are shown for a compound of the series studied. In this experiment, not only thermal dilatation and recovery effects are compensated but the elastic response is separated from viscous flow (cf. Equ. 3). The shift of the transitions of a series of such blends by systematically varying their composition has been successfully studied by the pulsed-load thermomechanical technique[16].

Figure 8. shows a series of derivatives of plasticized PVC-ethylene vinylacetate blends containing the same amounts of plasticizer but different amounts of ethylene-vinylacetate copolymer. These curves were obtained from the temperature dependence of isochronous elastic compliances measured by the pulsed load technique in compression after a load-time of 3.1 s. In the temperature range of the transition the irreversible »plastic« part was negligible.

Besides thermally stimulated creep (or stress relaxation), transitions can be very efficiently detected by thermally stimulated recovery. As an example, in Figure 9. thermally stimulated recovery curves of a plasticized PVC compound are shown after stretching the samples at different temperatures by 5.5% and then quenching them. In this experiment strains frozen-in by processing have been erased by annealing at 150 °C. The heterogeneous nature of the glass transition is clearly indicated by the thermally stimulated recovery curves. By stretching the sample at low temperature (—1 °C), only a small part of the total relaxation time distribution is frozen-in and re-activated by heating. The corresponding transition is narrow, it can be fairly well

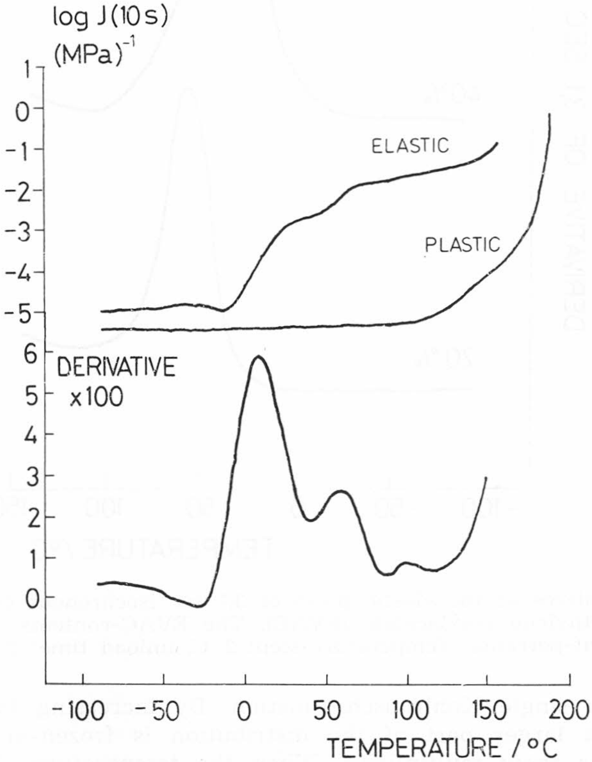

Figure 7. A typical compressional pulsed-load thermomechanical creep curve for a 60:20:20 PVC-di-iso-octyl phthalate-ethylene vinylacetate copolymer blend. Load time: 10 sec, temperature-step 2 °C, unload period: 2 min.

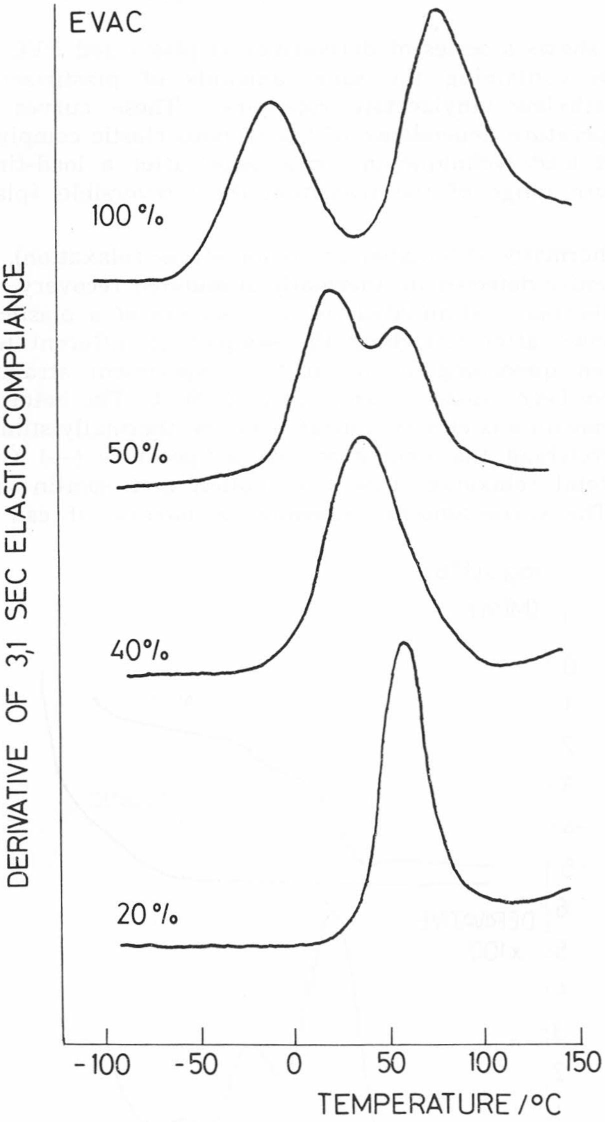

Figure 8. Derivatives of the elastic parts of 3.1 sec isochronous compliances of a series of PVC-ethylene vinylacetate (EVAC). The EVAC-contents are indicated in weight-percents. Temperature-step: 2 °C, unload time: 2 min.

described by a single Kohlrausch function. By increasing the temperature of stretching a larger part of the distribution is frozen-in: the resulting recovery curves show multiplicity. When the temperature of stretching is sufficiently high, almost all the frozen-in deformation, 5.5%, is recovered and several transition bands appear. Such a multiplicity of the glass-transition band was also found by thermally stimulated creep (cf Figure 6. and ref. 15) but the thermally stimulated recovery method was found most efficient in studying such »inhomogeneously broadened« transition bands.

Figure 10 shows such an experiment on unplasticized PVC in which a thermally stimulated recovery measurement is done in two steps. The sample was stretched at 150 °C and quenched. After this, thermally stimulated recovery was measured up-to a certain temperature (100 °C) and then quenched again. By this a part of the frozen-in relaxation spectrum was released. By

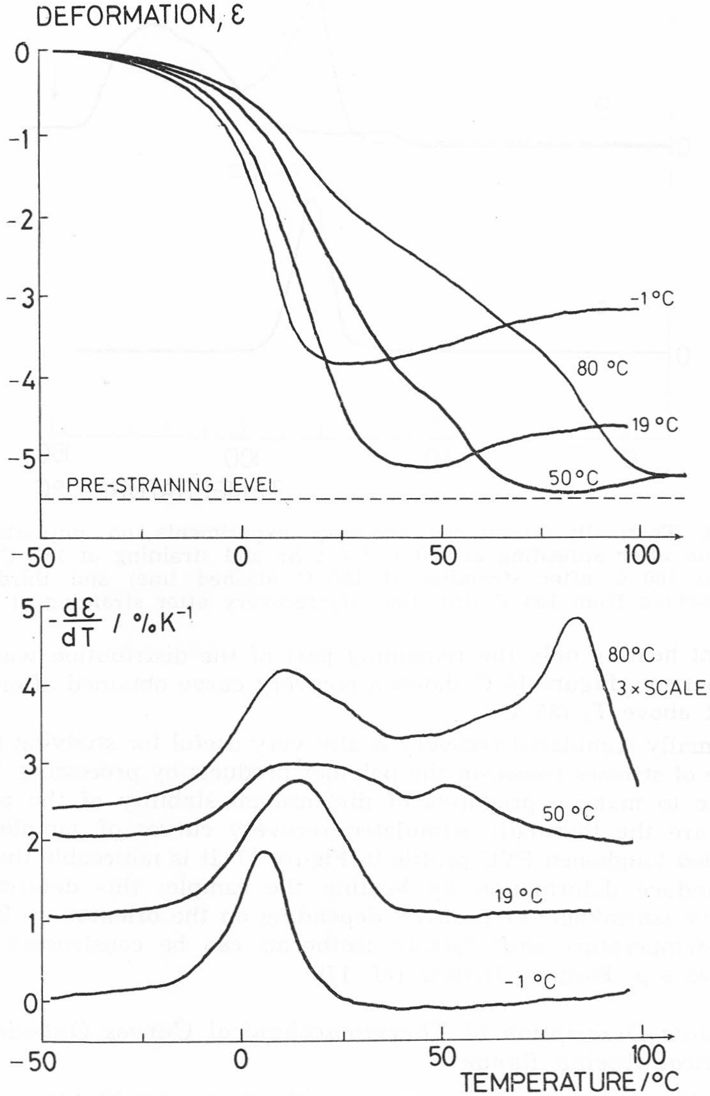

Figure 9. Thermally stimulated recovery (shrinkage) curves for a plasticized PVC-compound measured after stretching the sample at different temperatures indicated. The sample was previously annealed for 1 hour at 160 °C. Rate of heating: 1 °C/min.

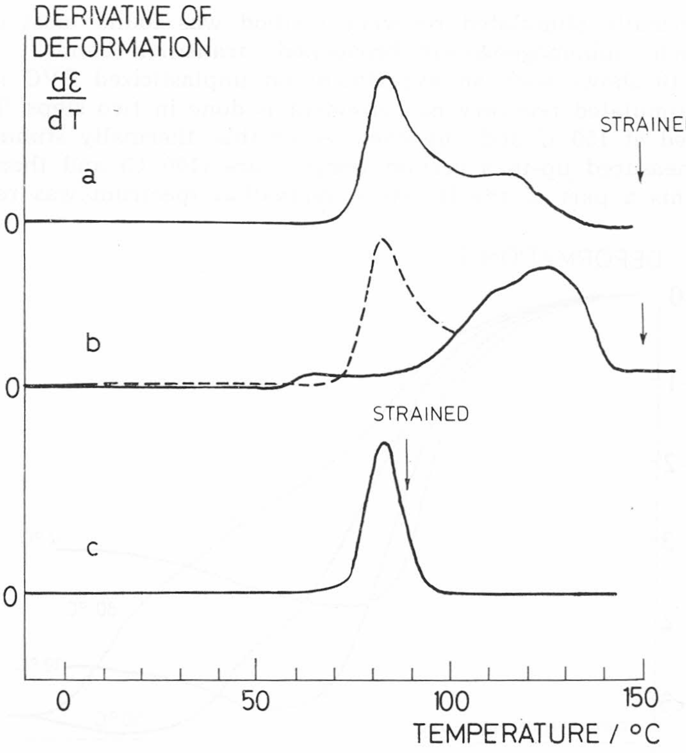

Figure 10. Thermally stimulated recovery experiments on unplasticized PVC. (a) first run after annealing at 160 °C for 1 hr and straining at 150 °C (b), second run up to 100 °C after straining at 150 °C (dashed line) and third run after quenching from 100 °C (full line) (c) recovery after straining at 86 °C.

subsequent heating only the remaining part of the distribution was activated. For comparison, Figure 10 C shows a recovery curve obtained after quenching from just above T_g (85 °C).

Thermally stimulated recovery is also very useful for studying the kinetics of release of stresses frozen-in the polymer products by processing. This makes it possible to make a prognosis of dimensional stability of the product. An example are the thermally stimulated recovery curves of samples cut from an extruded toughened PVC profile in Figure 11. It is noticeable that frozen-in stresses induce deformation by heating the sample; this deformation may be negative (shrinkage) or positive, depending on the orientation. By knowing the time-temperature shift factors, isotherms can be constructed from such curves (see e. g. Forgács, Hedvig ref. 17).

Quantitative Description of Thermomechanical Curves Outside the Physical Ageing Range

In order to describe thermomechanical curves quantitatively the temperature dependence of the time-temperature shift factor must be known. In most cases it can be expressed by the WLF-function (Equ. 9), so in order to calculate the effective time the knowledge of the two WLF constants

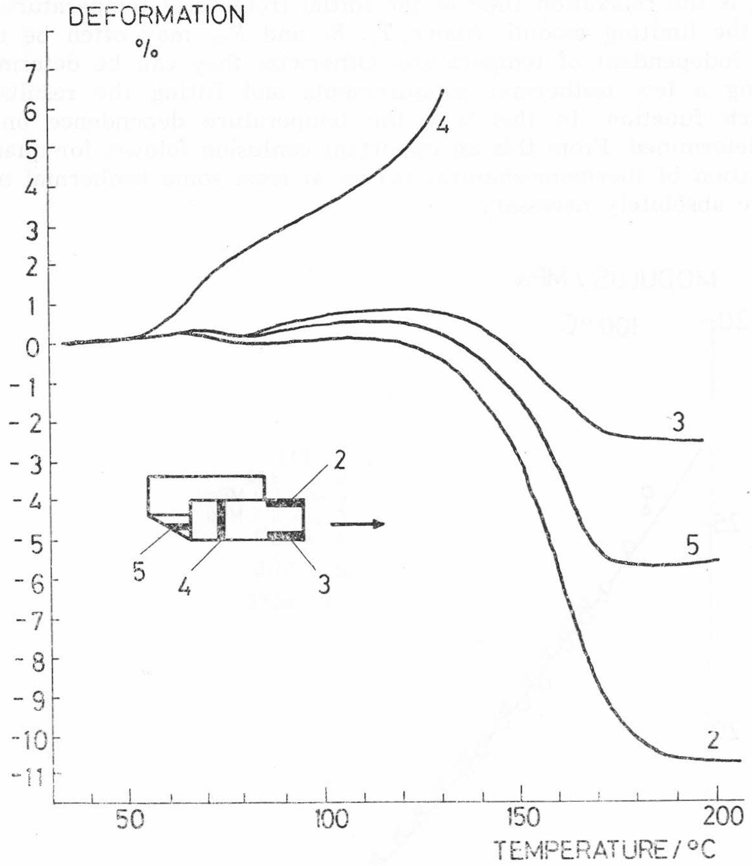

Figure 11. Thermally stimulated recovery of samples cut from a PVC profile in different directions shown in the insert.

A_T and B_T is sufficient. Thus, the effective time (sec) in the (7) Kohlrausch function is expressed as

$$t_e(T) = \frac{1}{r} \int_{T'=T_0}^{T} \left[\exp \left\{ \frac{A(T'-T_0)}{B+T'-T_0} \right\} \right]^{-1} dT' \tag{21}$$

where T_o is the initial temperature, which is also the reference temperature for A_T and B_T is the rate of heating, K/sec.

The exponent N of the Kohlrausch function (Equ. 7) is found in good approximation constant above T_g. If necessary, its temperature dependence can be taken into account. Thus the thermally stimulated stress relaxation can be described as

$$E(T) = E_\infty + (E_o - E_\infty) \exp \left[- \left(\frac{t_e}{\tau_o} \right) \right] \tag{22}$$

where τ_o is the relaxation time at the initial (reference) temperature, E_o and E_∞ are the limiting moduli. Above T_g, E_o and E_∞ may often be regarded as being independent of temperature. Otherwise they can be determined by performing a few isothermal measurements and fitting the results to the Kohlrausch function. In this way the temperature dependence on N can also be determined. From this an important conlusion folows: for quantitative interpretation of thermomechanical curves at least some isothermal measurements are absolutely necessary.

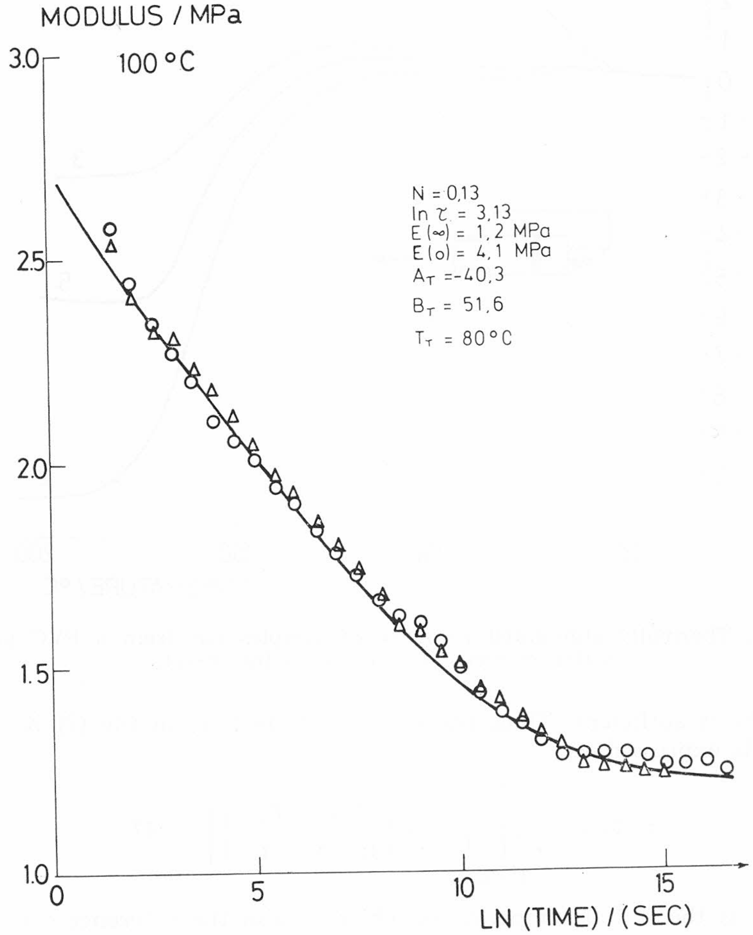

Figure 12. Stress relaxation master curve of a plasticized PVC-compound obtained from a series of isotherms (circles) and from trasformation of thermally stimulated stress relaxation curve (triangles). The full line represents the Kohlrausch function fitted to the data. Strain: 4—6%.

In order to check the validity of Equ. (22), thermaly stimulated stress relaxation of a plasticized PVC-compound was measured together with some isotherms above T_g. From the isotherms a master-curve was constructed and the WLF constants determined. The individual isotherms, as well as the master curve, were fitted to the Kohlrausch function and the parameters E_o, E_∞, τ_o and N determined. Then, with the same material, a thermally stimulated stress relaxation curve was measured and transformed into isotherms by using the effective time according to Equ. (21). Figure 12. shows the master curve (circles), the curve transformed from the thermally stimulated stress relaxation measurement (triagles) and also the corresponding Kohlrausch curve (full line). The main parameters are also indicated in Figure 12. It is seen that the agreement is fair.

Thermomechanical Measurements in the Range of Physical Ageing

In the glassy state creep and stress relaxation is governed by the storage time (history) of the sample, as well as by temperature. The initial condition is set by the effective storage time depending on the thermal history of the sample. During a thermomechanical measurement the elapsed time would make relaxation times longer while temperature increase would shorten them. Besides, an increase in temperature would erase a part of the thermal history resulting in shift relaxation times down. This makes interpretation of thermomechanical curves in the range of physical ageing rather complex. In fact, in this range, creep curves obtained by linear increase of temperature can be hardly termed as »thermally stimulated« because the effect of the elapsed time to the relaxation times is usually larger than that of the temperature. Application of the concept of effective time for transforming the temperature to time-scale below without considering physical ageing, correspondingly, leads to serious errors. This is also true of the dynamic mechanical result. In unplasticized PVC the range of physical ageing is from —50 ° to 80 °C (T_g).

In order to obtain the time-temperature shift factor, the history of the sample has to be erased by annealing above T_g. Then, before the measurement of isotherms, the sample should be stored at the temperature of the measurement for a fixed time $t_{so} >$ the total time of the measurement. In this way the history is fixed, the time-temperature shift factor can be determined in usual way: by horizontal and eventually vertical shifts.

Figure 13. shows a stress relaxation master curve for unplasticized polyvinylchloride below T_g obtained in this way. The temperature dependence of the shift factor is shown in Figure 14. in an Arrhenius representation. It is seen that from $T_g \approx 80$ °C down to 40 °C there is an Arrhenius dependence with activation enthalpy of 170 kJ/mol. Below 40 °C the temperature dependence becomes very weak with small virtual activation enthalpy ($\approx$ 25 kJ/mol). In this temperature range, the temperature-dependence of $\ln a_T$ is approximately linear, which is in agreement with that found by Struik[11] by creep experiments.

In order to extrapolate stress relaxation data to long times, the Kohlrausch function with the effective time corresponding to continuous physical ageing was used (Equ. 14). The reason is that at times higher than t_s physical ageing runs along with stress relaxation slowing it down.

Figure 15 shows a typical set of isothermal stress relaxation curves fitted to the Kohlrausch function without considering simultaneous physical ageing (dashed lines) and by considering it according to Equ. 14 (full lines). The

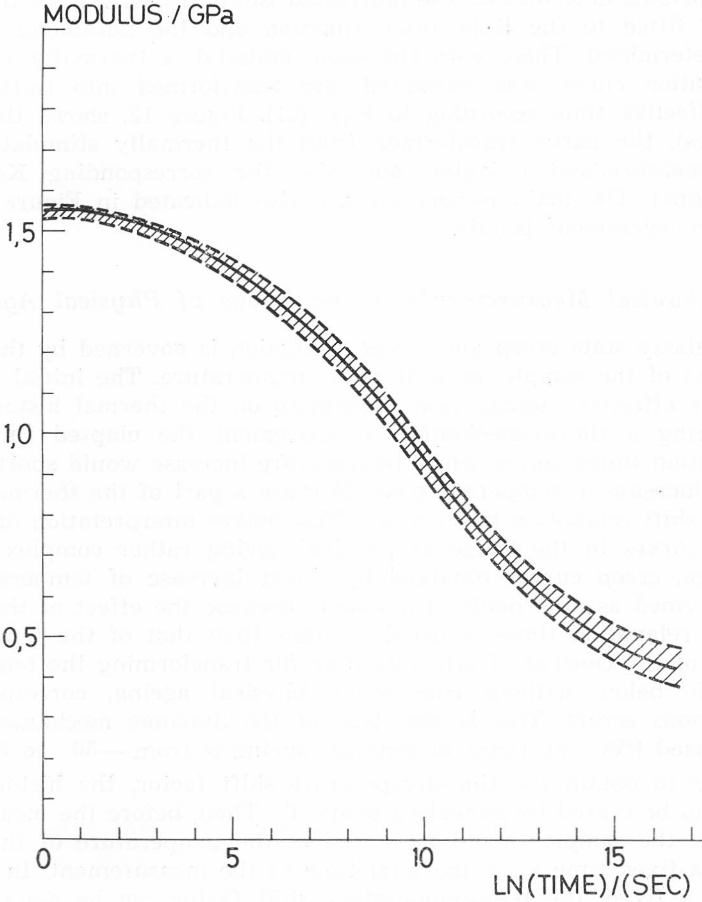

Figure 13. Stress relaxation master curve of unplasticized polyvinylchloride in the physical ageing range constructed from isotherms measured after storage time of 17 hrs after quenching from 100 °C. The full line is a Kohlrausch function fit observing simultaneous ageing; dashed area shows 95% confidence-limit. Strain: 0.6—0.8%.

experimental curve is represented by circles. In this experiment the storage time t_s was 17 hours, the time of the experiment was from 1 sec up to 5 hours (»experimental window«). Only a few temperatures are shown for clarity. It is noticeable that simultaneous physical ageing becomes effective at times exceeding the storage time t_{so}. Extrapolated values to long times are shown to deviate very strongly from those obtained by not considering simultaneous physical ageing. Similar results were obtained by creep experiments.

By fitting the Kohlrausch function to experimental creep — and stress relaxation — data, under the conditions of simultaneous physical ageing, the

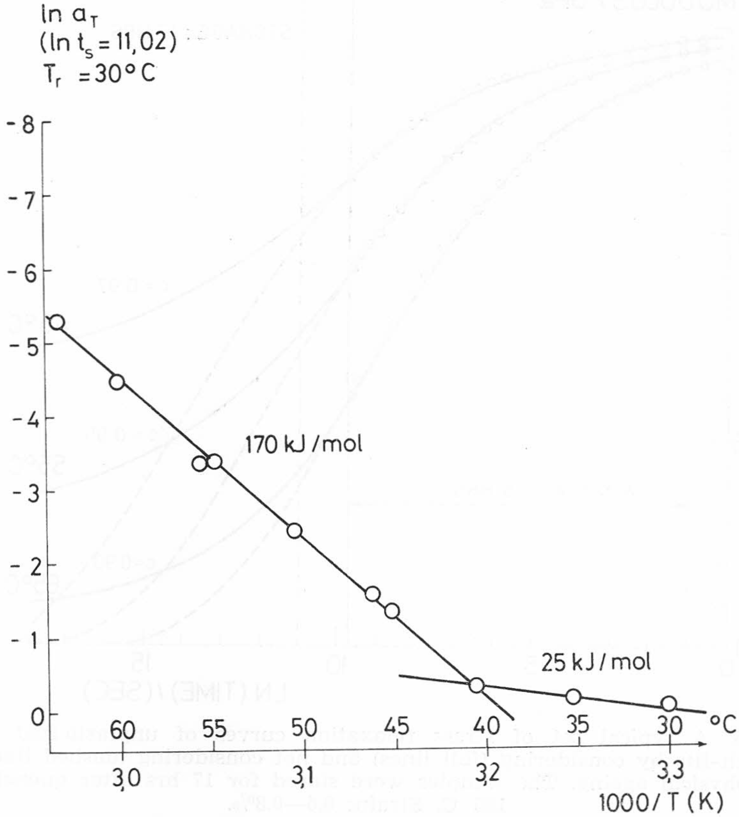

Figure 14. The temperature dependence of the time-temperature shift factor of unplasticized PVC in the physical ageing range obtained from tensile stress relaxation experiments measured at the same storage times of 17 hrs.

shift rate $C(T)$ must be known. This was determined by doing isothermal measurements by changing the storage time t_s.

The shift rate is simply obtained as

$$\ln a_\delta (t_s, t_{sr}) = c(T) [\ln t_s - \ln t_{sr}] \tag{23}$$

where t_{sr} is a reference storage time at temperature T. $c(T)$ values obtained in this way are also indicated on Figure 15.

The fitting procedure, thus, involves four parameters: in the case of stress relaxation $E(o)$, $E(\infty)$, N and $\ln \tau$ (cf. Equ. 22). By this procedure »vertical« shift problems are accounted for.

In the case of thermomechanical measurements the knowledge of parameters $E(o, T)$, $E(\infty, T)$,$N(T)$ and $c(T)$ is, however, not sufficient for interpretation of the results because an increase of temperature is known to erase the history-effect, resulting in shifting the relaxation time distribution to shorter times[11]. When t_s is long, this may look as thermal stimulation; at least up to a certain temperature. The time needed for complete erasure of the history is expressed as[11]

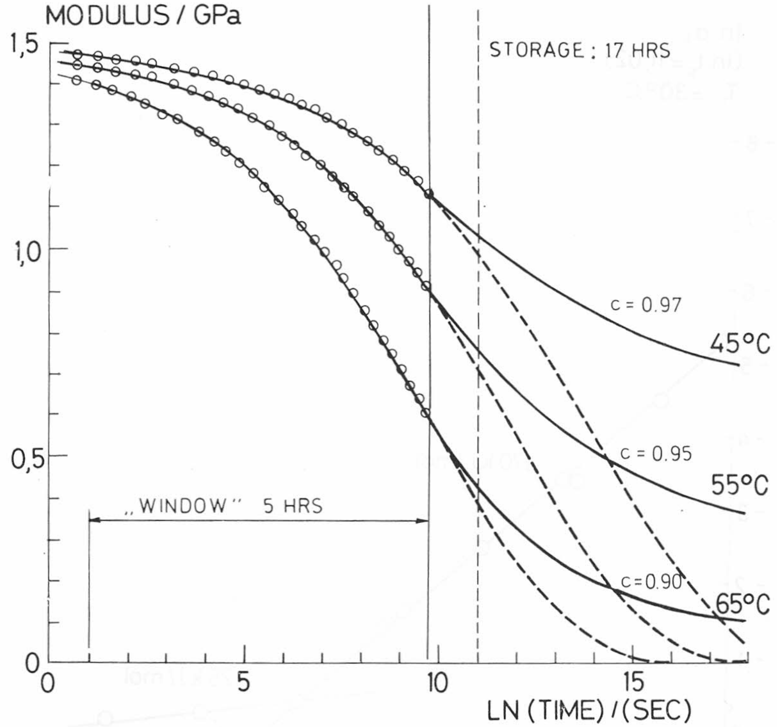

Figure 15. A typical set of stress relaxation curves of unplasticized PVC and Kohlrausch-fits by considering (full lines) and not considering (dashed lines) simultaneous physical ageing. The samples were stored for 17 hrs after quenching from 100 °C. Strain: 0.6—0.8%.

$$t_m = t_{so}\, k \exp\left[\frac{H}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right] \tag{24}$$

where t_{so} is the storage time (below T_g) at temperature T_o, T is the changing temperature, k is a materials constant (for PVC $k = 0.34$), H is the activation enthalpy of the process, (for PVC H = 160 kJ/mol) R is the gas constant.

By constant load thermally stimulated creep or-stress relaxation measurements in the physical ageing range by increasing temperature the relaxation time is first shifted to shorter times until t_m is reached. After that, simultaneous physical ageing would shift relaxation times upward while thermal stimulation would shift them down, continuously making the overall result rather complex.

It is easier to analyze pulsed-load thermomechanical curves obtained by the stepwise temperature program, as shown in Figure 3, especially if the chosen initial storage time t_{so} is short enough to be erased in the first temperature step. In the subsequent steps the storage time corresponding to the unload-period may be partly or totally erased. In this case, the effective time of simultaneous physical ageing according to Equ. (14) can be used in each load-pulse to calculate the isochronous moduli or compliances.

When, on the other hand, the initial storage time t_{so} is very long, in the load-periods the moduli (or compliances) will be constant over a wide temperature range and decrease (increase) only when the temperature approaches T_g. In this case, the measured isochronous values are near to the limiting $E(o)$ i. e. $J(o)$ »unrelaxed« ones.

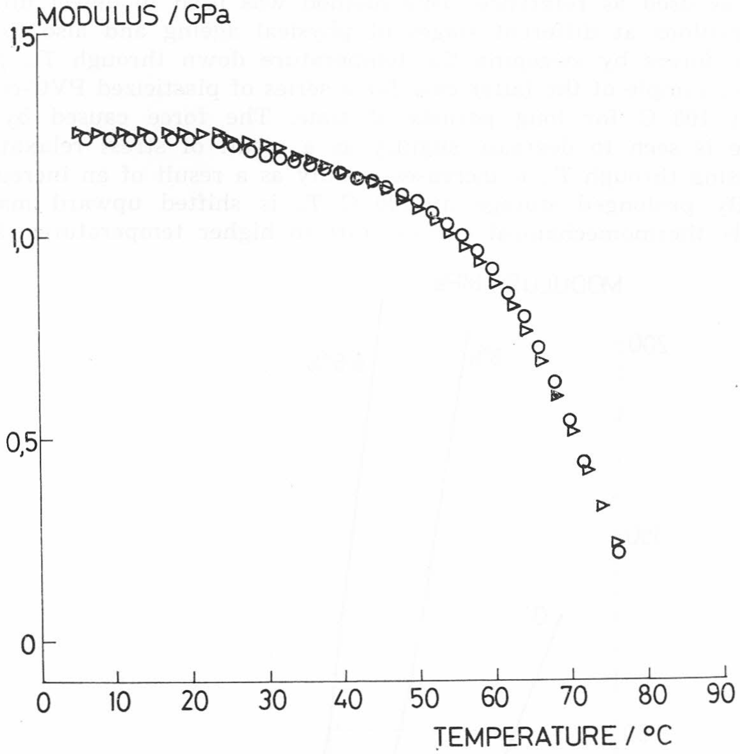

Figure 16. 12 sec differential thermally stimulated stress relaxation curve (elastic part) of unplasticized PVC in the physical ageing range. Storage time after quenching from 100 °C: 18 hrs. Temperature step: 2 C unload period 6 min, strain 0.7%. Symbols ○ and △ mean different samples.

Figure 16. shows a typical pulse-load stress relaxation curve of unplasticized PVC in the physical ageing range, measured after storage at the lowest temperature for 18 hours. The reversible (elastic) part of the 12 sec isochronous modul is plotted as a function of the temperature. The isochronous moduls is found approximately constant in the initial temperature range, its value being near to the $E(o)$-limit. By approaching T_g the isochronous modulus decreases because the relaxation times are decreased by thermal stimulation and by erasure of the thermal history of the sample. At low temperatures this erasing effect is small, the relaxation time is governed mainly by the storage-time. By increasing temperature the erasing effect makes relaxation times decrease until history is completely erased and the relaxation time is determined by the unload-periods. After this, the temperature dependence of the isochronous modulus is determined by that of the shift-rate $c(T)$, which falls rapidly by approaching T_g.

Thermal Dilatation Effects

The differential technique makes it possible to measure thermal dilatation with high accuracy. In such measurements a metal of known dilatation coefficient was used as reference. This method was used to detect dilatometric glass-transitions at different stages of physical ageing and also to measure shrinkage forces by sweeping the temperature down through T_g. Figure 17 shows an example of the latter case for a series of plasticized PVC-compounds stored at 100 °C for long periods of time. The force caused by thermal shrinkage is seen to decrease slightly as a result of stress relaxation, then after passing through T_g, it increases rapidly as a result of an increase of the modul. By prolonged storage at 100 °C T_g is shifted upward making the »inverted« thermomechanical curves shift to higher temperatures. Since the

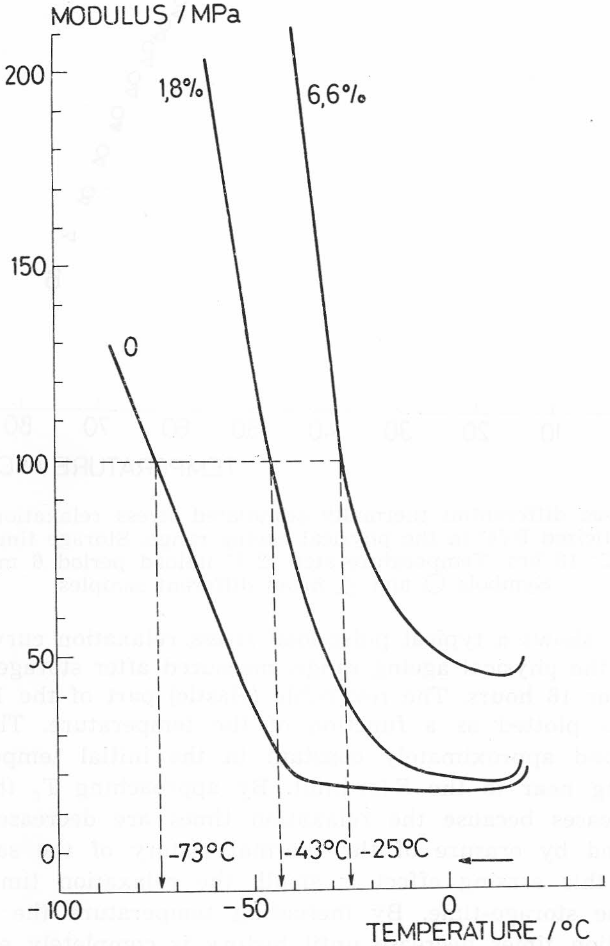

Figure 17. Stress-relaxation mode thermomechanical curves measured by decreasing temperature for a plasticized PVC compound at different stages of annealing at 100 °C. The loss of weight (%) is indicated. Limiting temperatures corresponding to 100 MPa are also indicated. Rate of cooling: 1 °C/min.

contraction which would be caused by cooling, if the lenght of the sample were not fixed, is measured simultaneously in the reference channel of the MULTIRELAX device, the modulus can be calculated.

Construction of Frequency-Domain Spectra

Finally, as an example of the transformation of time-domain (or temperature-domain) creep or stress-relaxation curves Figure 18 shows a creep-

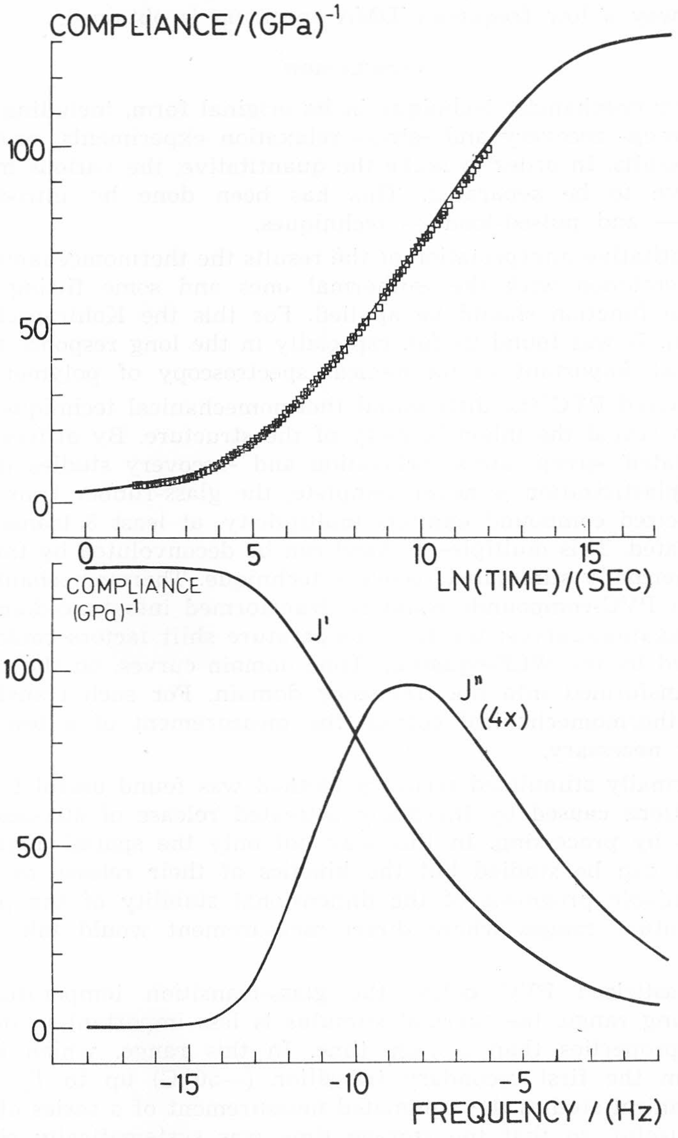

Figure 18. Transformation of a time-domain creep curve of a plasticized PVC-compound to the frequency-domain. J' is the storage, J'' is the loss-compliance. Full line in the time domain curve is a Kohlrausch fit with $\ln \tau = 8$, $N = 0.32$.

-master curve of a plasticized PVC-compound and its transforms to storage- and loss moduli as a function of the frequency. The transformation was performed by using the Struik-Schwarzl equations (15). As mentioned before, the master curve can be constructed by performing a few isothermal and a thermally stimulated creep measurement. This was done in the present case. Another possibility is to select a fixed angular frequency ω_o to which, according to Equ. (15), a fixed creep time t_o corresponds and measure creep by stepwisely increasing temperature up-to creeep times of 5.76 t_o (cf. Equ. 15). In this way a low frequency DMA spectrum is obtained.

CONCLUSION

The thermomechanical technique in its original form, including thermally stimulated creep- recovery and -stress relaxation experiments, provides only qualitative results. In order to make the quantitative, the various mechanisms involved have to be separated. This has been done by introducing the differential — and pulsed-load — techniques.

For quantitative interpretation of the results the thermomechanical method has to be combined with the isothermal ones and some fitting procedure to a response function should be applied. For this the Kohlrausch response function (Equ. 7) was found useful, especially in the long response time range which is most important in mechanical spectroscopy of polymers.

In plasticized PVC the differential thermomechanical technique has made it possible to reveal the inhomogeneity of the structure. By differential thermally stimulated -creep -stress relaxation and -recovery studies it has been shown that plasticization is never complete, the glass-rubber transition band of the plasticized compound exhibits multiplicity, at least 3 transition bands can be separated. This multiple- T_g band can be deconvoluted by the »thermal sampling« thermally stimulated recovery technique. Thermomechanical curves of plasticized PVC-compounds could be transformed into time-domain creep- or stress relaxation-curves; the time-temperature shift factors could be fairly well described by the WLF-equation. Time domain curves, on the other hand, could be transformed into the frequency domain. For such transformations, besides the thermomechanical curves, the measurement of a few isotherms is absolutely necessary.

The thermally stimulated recovery method was found useful for studying the deformations caused by thermally activated release of stresses frozen-in the products by processing. In this way not only the spatial distribution of such stresses can be studied but the kinetics of their release as well. This enables a reliable prognosis of the dimensional stability of the products in such temperature ranges where direct measurement would take too much time.

In unplasticized PVC below the glass-transition temperature in the physical ageing range, the thermal stimulus is less important in determining mechanical properties than storage time. In this range, which is believed to start form the first secondary transition (—50 °C) up to T_g, instead of thermomechanical studies the automated measurement of a series of isotherms was found useful, so that the storage time was systematically changed. In order to obtain time-temperature shift factors in the physical ageing range, the storage time at each temperature is to be rigorously kept constant.

REFERENCES

1. V. A. Kargin, G. L. Slonimsky, *Doklady A. N. SSSR* **62** (1948) 239.
2. J. C. Monpagens, D. G. Chatain, C. Lacabanne, P. G. Grautier, *J. Polymer Sci. Polym. Physics Ed.*, **15** (1977) 767.
3. P. Hedvig, *Macromolecular Reviews, J. Polymer Sci.* **15** (1980) 375.
4. *Einführung in die Thermodynamik der Irreversiblen Processe,* H. A. Baur, Darmstadt, Wiss. Buchgesellschaft, 1984.
5. *Non-equilibrium Statistical Thermodynamics,* in Russian, D. N. Zoubarov, Moscow, Izd. Nauka, 1971.
6. I. L. Hopkins, R. V. Hamming, *J. Applied Physics* **28** (1975) 960.
7. See in: *Elastic and Creep Properties of Filamentous Materials and Other High Polymers,* H. Leaderman, The Textile Foundation Washington D. C. 1944 p. 13.
8. F. Gény, L. Monnerie, *J. Polym. Sci., Polym. Phys. Ed.* **15** (1977) 1.
9. *Dielectric Relaxation in Solids,* A. K. Jonscher, London Chelsea Dielectric Press, 1983.
10. A. J. Kovacs, *Macromol. Chem. Suppl.* **2** (1979) 81.
11. *Physical Aging in Amorphous Polymers and Other Materials,* L. C. E. Struik, Amsterdam, Oxford, New York, 1978 Elsevier Sci. Publ. Co.
12. *Anelastic and Dielectric Effects in Polymeric Solids* N. G. McCrum, B. E. Read, G. Williams, J. Wiley Sons London, New York, Sidney 1967.
13. *Dielectric Spectroscopy of Polymers,* P. Hedvig, Bristol Adam Hilger Ltd., 1977.
14. L. C. E. Struik, F. R. Schwarzl, *Rheologica Acta* **8** (1969) 134.
15. E. Földes, P. Hedvig, J. Vinyl, *Technology* **3** (1981) 111.
16. P. Hedvig, K. Marossy, *Die Angew. Makromol. Chemie* **97** (1981) 51.
17. P. Forgacs, P. Hedvig, *J. Polymer Sci.* **58** (1977) 77.

SAŽETAK

Kvantitativna termomehanička analiza smjesa poli(vinilklorida)

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Proučavane su neomekšane i omekšane PVC-mješavinei smjese PVC/omekšivač/etilen-vinilacetat-kopolimer primjenom nove diferencijalne termomehaničke tehnike, mjerenjem termički stimuliranog i izotermičkog puzanja, povratne deformacije ili relaksicaje naprezanja paralelno s neopterećenim uzorkom. Raspravlja se o mogućnosti kvantitativne interpretacije takvih diferencijalnih termomehaničkih krivulja unutar i izvan temperaturnog fizičkog starenja. Diferencijalnom tehnikom puzanje je odvojeno od termičkog širenja i povratne deformacije; tehnikom pulsnog opterećenja povratno puzanje odvojeno je od ireverzibilnog tečenja. Tim je metodama nađeno da omekšane PVC-smjese pokazuju višestruka stakišta, koja se ne mogu opaziti konvencionalnim tehnikama, kao što su diferencijalna pretražna kalorimetrija, dinamička mehanička analiza ili nuklearna magnetska rezonancija. Kohirauschova funkcija odziva i metoda efektivnog (reduciranog) cremena omogućuju transformaciju termomehaničkih krivulja »temperaturnog područja« u krivulje vremenskog područja, koje se, pak, mogu transformirati u spektre frekvencijskog područja. Pored termomehaničkih krivulja za izvođenje transformacije potrebno je i nekoliko izotermnih krivulja. U temperaturnom rasponu fizičkog starenja termička stimulacija prekrivena je efektom stanja i proteklog vremena, koji pomiče raspodjelu prema duljim vremenima. Nađeno je da je u tom području tehnika pulsnog opterećenja s temperaturnom kontrolom u koracima vrlo korisna, budući da temperaturni koraci mogu potpuno ili djelomično izbrisati efekte prethodne historije. Diferencijalna je tehnika također upotrijebljena pri proučavanju višestrukih stakišta u blendima PVC-di-izo-oktilftalata i etilen-vinilacetat-kopolimera.