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THE APPLICATION OF CERTAIN MEMORY FUNCTIONS TO THE DESCRIPTION OF LINEAR VISCOELASTICITY OF SOLID POLYMERS

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The work presents the applicability of the exponential–type functions to the description of linear viscoelasticity in polymers. These functions can be treated as memory functions and are applied to the constitutive equations which consist of the Volterra integrals. The equations are included in the theory of viscoelasticity which is mathematically coherent. This enables the evaluation of all functions neccesary to describe a viscoelastic body such as spectra, components of complex modulus and compliance, etc. A new memory function competitive to the ones previously used is introduced in this work.
The suggested description is verified with the help of complex rheological tests. The numerical values of the parameters in the constitutive equations are calculated based on a simple creep test. To verify these values, another type of rheological test is applied and the obtained, experimental curves are compared with numerical simulation based on the formerly calculated parameters.
Apart from the purely phenomenological verification, a comparison is made between the molecular weight distribution curves and the curves calculated from the newly introduced memory function. A good convergence of the curves which simulate the rheological processes as well as the spectral curves with the experimental results confirms the proper structure of the function.

1. Introduction

Polymers are viscoelastic materials. That is why the calculating methods usually applied to classic materials like metals cannot be used for engineering calculation of strength of plastic elements. In order to perform the calculations in a proper way, an appropriate description of linear viscoelasticity should be established. This kind of description consists of constitutive equations which contain the so called memory functions. Finding a proper form of those functions is a complicated mathematical task.

The attempts to create this kind of description were intensively undertaken in the sixties. Due to the serious mathematical difficulties which arose, many authors gave up this method and switched into purely numerical solutions. Thus this question remains open so far.

This paper presents the critical analysis of the memory functions known in the literature and introduces a new, original function named "root function". The purpose of this paper is to demonstrate the possibilities of the new function and to remind the potentials of the analytical methods which seem to be forgotten. The theoretical assumptions have been verified by the static rheological tests performed at a complex program of load.

2. Theory

A classic, linear–viscoelastic, isotropic body can be described by two alternative forms of the constitutive equation

$$e_{ij}(t) = \frac{s_{ij}(t)}{2G} + \frac{\omega}{2G}\int\limits_0^t \Phi(t-u)s_{ij}(u)du \tag{2.1}$$

$$s_{ij}(t) = 2Ge_{ij}(t) - 2G\omega\int\limits_0^t \Psi(t-u)e_{ij}(u)du \tag{2.2}$$

where

$e_{ij}(t)$ – shear strain

$s_{ij}(t)$ – shear stress

G – parameter related to the Kirchoff modulus

ω – parameter

$\Phi(t)$ – memory function of creep

$\Psi(t)$ – memory function of relaxation.

The description given above represents the deviatoric component of the stress and strain tensors. For the hydrostatic component the description is analogous and shall not be quoted.

The mutual relation between the memory functions $\Phi(t)$ and $\Psi(t)$ can be obtained by applying Laplace transform to both equations (2.1) and (2.2). The result is

$$\bar{\Psi}(p) = \frac{\bar{\Phi}(p)}{1+\omega\bar{\Phi}(p)} \tag{2.3}$$

Constitutive equations (2.1) and (2.2) enable us to define certain distribution functions $\Lambda(s)$ and $\Pi(s)$ as

$$\Phi(t) = \int\limits_0^\infty \Lambda(s)s\exp(-st)ds \tag{2.4}$$

$$\Psi(t) = \int_0^\infty \Pi(s) s \exp(-st) ds \tag{2.5}$$

where $\tau = 1/s$ is a characteristic time constant. Distribution functions $\Lambda(s)$ and $\Pi(s)$ are related to the spectra of creep $f(\tau)$ and relaxation $g(\tau)$ respectively by the formulae

$$f(\tau) = \frac{\omega}{2G} s^2 \Lambda(s) \tag{2.6}$$

$$g(\tau) = 2G\omega s^2 \Pi(s) \tag{2.7}$$

Eqs (2.6) and (2.7) enable us to find the correlation between the phenomenological behaviour of the material and the structure of it.

We may convert the τ–scale into the M–scale (M–molecular weight) utilizing the well known formula

$$\tau = \lambda M^k \tag{2.8}$$

In such a case, new function $f(M)$, in accordance with formula (2.6), will be equivalent to the molecular weight distribution function $D(M)$. Usually it is assumed that $k = 2 - 3.5$, $\lambda = 1$.

Function $D(M)$ is normalized to unity

$$\int_0^\infty D(M) dM = 1 \tag{2.9}$$

Thus the integral of the equivalent function $f(M)$ should also be convergent to a finite value

$$\int_0^\infty f(M) dM < +\infty \tag{2.10}$$

By applying a normalizing coefficient, convergence to unity can be obtained.

Substituing Eq (2.8) into Eq (2.6) we obtain the definite relation between the distribution function $\Lambda(s)$ and the molecular weight distribution function $f(M)$

$$f(M) = \frac{\omega}{2G} \frac{1}{M^{2k}} \Lambda\left(\frac{1}{M^k}\right) \tag{2.11}$$

If a viscoelastic material undergoes dynamic vibration, it can be characterized by the complex shear modulus G^x. Its real component is related to the storage of energy, its imaginary component – to the loss of energy. Complex modulus is obtained by applying the formula

$$G^x(n) = \lim_{t \to \infty} \frac{s_{ij}(t)}{e_{ij}(t)} \tag{2.12}$$

where $e_{ij}(t) = e_{ijo}(t) \exp(int)$ (n – frequency), $s_{ij}(t)$ is calculated by substituing for $e_{ij}(t)$ described by the given formula into Eq (2.2) and by performing the integration.

3. Creating memory functions

Searching for new memory functions is the main theoretical problem of linear viscoelasticity. These function should meet certain requirements which can be listed as follows

- should be relatively uncomplicated
- should be positive and monotonically decreasing to zero
- their integrals should be convergent to a finite value
- their Laplace transform should be uncomplicated
- calculation of the related viscoelastic functions (moduli, spectra) should be possible
- should be "flexible" i. e. easy fitted to the experimental data
- their numerical tabulation should be effective.

The additional requirement is that the related MWD (molecular weight distribution) function should have the desired character of plot i.e. it should increase from zero for $M = 0$ to a maximum and then decrease to zero for $M \to \infty$. In addition, the integral of this function should be convergent to a finite value (Eq (2.10)).

To fulfill all the listed requirements simultaneously is a difficult task. Mutual recalculation of $\Phi(t)$ and $\Psi(t)$ is in most cases the main obstacle.

All the requirements are met by the exponential function $\Phi(t) = \alpha\exp(-\alpha t)$. Its application was described elsewhere (cf [3,4,5,6]). So far most of the functions suggested in the literature is derived from the exponential function. This is why they are called "generalized" or "stretched exponential" functions.

3.1. Fractional function

A simple exponential function can be represented by the series

$$\alpha\exp(-\alpha t) = -\alpha\sum_{m=1}^{\infty}(-1)^m\frac{(\alpha t)^{m-1}}{(m-1)!} \tag{3.1}$$

If we introduce Euler function $\Gamma(m) \doteq (m-1)!$ into Eq (3.1), it can be rewritten as

$$e_{\nu\alpha}(t) = -\alpha\sum_{m=1}^{\infty}(-1)^m\frac{(\alpha t)^{m\nu-1}}{\Gamma(m\nu)} \tag{3.2}$$

where $0 < \nu < 1$.

This function called fractional function was worked out by Wilczyński [9,10] on a Mittag–Leffleur function [11] as the theoretical basis.

In practical application the integral of the fractional function is often used

$$e^*_{\nu\alpha}(t) = \int_0^t e_{\nu\alpha}(u)du = -\sum_{m=1}^{\infty}(-1)^{m-1}\frac{(\alpha t)^{m\nu}}{\Gamma(m\nu+1)} \tag{3.3}$$

The plots of both the fractional function $e_{\nu\alpha}(t)$ and its integral $e^*_{\nu\alpha}(t)$ are presented in Fig.1 and Fig.2. The figures let us assume that this function is very flexible.

Both the fractional function and its integral can be converted into the integral representations

$$e_{\nu\alpha}(t) = \frac{\alpha}{\Pi}\sin(\Pi\nu)\int_0^\infty \exp(-\alpha ut)\,\frac{u^\nu}{1+2u^\nu\cos(\Pi\nu)+u^{2\nu}}du \tag{3.4}$$

$$e^*_{\nu\alpha}(t) = 1-\frac{\sin(\Pi\nu)}{\Pi}\int_0^\infty \exp(-\alpha ut)\,\frac{u^{\nu-1}}{1+2u^\nu\cos(\Pi\nu)+u^{2\nu}}du \tag{3.5}$$

Papers [12,13,14] were applied while performing the conversion.

The asymptotic properties of the function are as follows

$$\lim_{t\to 0} e_{\nu\alpha}(t) = \infty \qquad \lim_{t\to 0} e^*_{\nu\alpha}(t) = 0$$

$$\lim_{t\to\infty} e_{\nu\alpha}(t) = 0 \qquad \lim_{t\to\infty} e^*_{\nu\alpha}(t) = 1$$

$$\int_0^\infty e_{\nu\alpha}(t)dt = 1 \qquad \bar{e}_{\nu\alpha}(p) = \frac{1}{1+\left(\frac{p}{\alpha}\right)^\nu}$$

The fractional function can be applied directly as a memory function

$$\Phi(t) = e_{\nu\alpha}(t) \tag{3.6}$$

$$\Psi(t) = \frac{e_{\nu\beta}(t)}{1+\omega} \tag{3.7}$$

where

$$\beta = \alpha(1+\omega)^{\frac{1}{\nu}} \tag{3.7a}$$

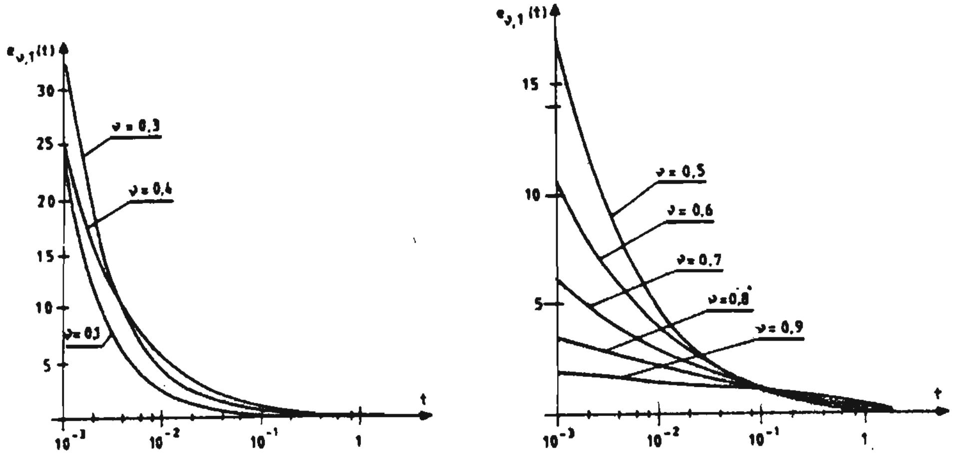

Fig. 1. Plots of the fractional function $e_{\nu\alpha}(t)$ for $\alpha = 1$

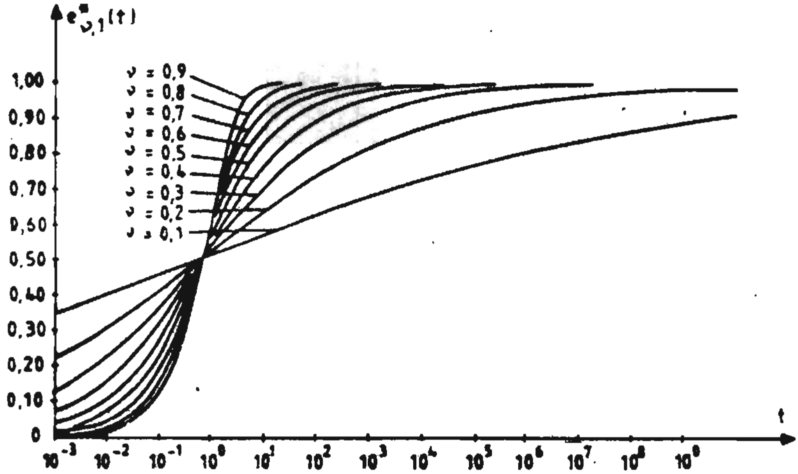

Fig. 2. Plots of the integral of the fractional function $e^{*}_{\nu\alpha}(t)$ for $\alpha = 1$

The memory functions represented by the given above formulae make it possible to determine the distribution functions $\Lambda(s)$, $\Pi(s)$ in the forms

$$\text{a)}\qquad \Lambda(s)=\frac{\sin(\Pi\nu)}{\Pi\alpha}\,\frac{\left(\frac{s}{\alpha}\right)^{\nu-1}}{1+2\left(\frac{s}{\alpha}\right)^{\nu}\cos(\Pi\nu)+\left(\frac{s}{\alpha}\right)^{2\nu}}$$

$$\text{b)}\qquad \Pi(s)=\frac{\sin(\Pi\nu)}{\Pi\beta(1+\omega)}\,\frac{\left(\frac{s}{\beta}\right)^{\nu-1}}{1+2\left(\frac{s}{\beta}\right)^{\nu}\cos(\Pi\nu)+\left(\frac{s}{\beta}\right)^{2\nu}} \tag{3.8}$$

It can be seen that both the functions are identical, they differ only in the shift of the argument.

The MWD–function, according to Eq (2.11) will be

$$f(M)=\omega\frac{\sin(\Pi\nu)}{2G\Pi\alpha}\,\frac{\left(\frac{1}{\alpha M^k}\right)^{\nu-1}}{1+2\left(\frac{1}{\alpha M^k}\right)^{\nu}\cos(\Pi\nu)+\left(\frac{1}{\alpha M^k}\right)^{2\nu}}\,\frac{1}{M^{2k}} \tag{3.9}$$

This function has the limits

$$\lim_{M\to 0} f(M)=\infty \qquad\qquad \lim_{M\to\infty} f(M)=0$$

so it is monotonic decreasing which does not fulfill the requirement concerning the character of plot. It is the main disadvantage of this function which has all advantages including flexibility.

The components of complex modulus and compliance can be presented in the form

$$J'(n)=\frac{1}{2G}\left[1+\omega\frac{1+\left(\frac{n}{\alpha}\right)^{\nu}\cos\frac{\Pi\nu}{2}}{1+2\left(\frac{n}{\alpha}\right)^{\nu}\cos\frac{\Pi\nu}{2}+\left(\frac{n}{\alpha}\right)^{2\nu}}\right] \tag{3.10}$$

$$J''(n)=\frac{\omega}{2G}\,\frac{\left(\frac{n}{\alpha}\right)^{\nu}\sin\frac{\Pi\nu}{2}}{1+2\left(\frac{n}{\alpha}\right)^{\nu}\cos\frac{\Pi\nu}{2}+\left(\frac{n}{\alpha}\right)^{2\nu}} \tag{3.11}$$

$$G'(n)=2G\left[1-\frac{\omega}{1+\omega}\,\frac{1+\left(\frac{n}{\beta}\right)^{\nu}\cos\frac{\Pi\nu}{2}}{1+2\left(\frac{n}{\beta}\right)^{\nu}\cos\frac{\Pi\nu}{2}+\left(\frac{n}{\beta}\right)^{2\nu}}\right] \tag{3.12}$$

$$G''(n)=2G\frac{\omega}{1+\omega}\,\frac{\left(\frac{n}{\beta}\right)^{\nu}\cos\frac{\Pi\nu}{2}}{1+2\left(\frac{n}{\beta}\right)^{\nu}\cos\frac{\Pi\nu}{2}+\left(\frac{n}{\beta}\right)^{2\nu}} \tag{3.13}$$

3.2. The attempts to generalize fractional function

There are many different possibilities to generalize the fractional function. Ržanicyn [15] suggested in 1968 to treat the transform (Eq (2.3)) in a particular way. If the transform of the memory function of relaxation $\bar{\Psi}(p)$ is assumed to be the transform of the new hypothetic memory function of a creep i.e. if we assume that $\bar{\Psi}(p) = \bar{\Phi}_1(p) = \bar{\Phi}(p)/(1+\omega\bar{\Phi}(p))$ and then if $\bar{\Phi}_1(p)$ is again substituted into Eq (2.3), the following result will be obtained

$$\bar{\Phi}_2(p) = \frac{\bar{\Phi}_1(p)}{1+\omega\bar{\Phi}_1(p)} = \frac{\bar{\Phi}(p)}{1+2\omega\bar{\Phi}(p)} \tag{3.14}$$

This substitution can be performed w–times. The so obtained transform of the new function can be written in the form

$$\bar{\Phi}_w(p) = \frac{\bar{\Phi}(p)}{1+w\omega\bar{\Phi}(p)} \tag{3.15}$$

where $\bar{\Phi}(p) = \bar{e}_{\nu\alpha}(p)$

The transform of the memory function of relaxation will be

$$\bar{\Psi}_w(p) = \frac{1}{1+(w+1)\omega}\,\frac{1}{1+\Big[\frac{p}{\alpha(1+(1+w)\omega)^{1/\nu}}\Big]^{\nu}} \tag{3.16}$$

The originals of this functions can be thus obtained

$$\Phi_w(t) = \frac{1}{1+w\omega}e_{\nu\gamma}(t) \tag{3.17}$$

$$\Psi_w(t) = \frac{1}{1+(1+w)\omega}e_{\nu\mu}(t) \tag{3.18}$$

where

$$\gamma = \alpha(1+w\omega)^{\frac{1}{\nu}} \tag{3.19}$$

$$\mu = \alpha[1+(1+w)\omega]^{\frac{1}{\nu}} \tag{3.20}$$

It can be seen that formulae (3.17), (3.18) end formulae (3.6), (3.7) respectively which represent the fractional function are similar.

The new w–parameter which appears in the latter function could increase its flexibility. The following analysis will prove, however, that this function is not a novelty if compared to the fractional function.

Formulae (3.17) and (3.18) can be rewritten in the symbolic form as

$$\Phi_w(t) = He_{\nu\gamma}(t) \tag{3.21}$$

$$\Psi_w(t) = \bar{H}e_{\nu\mu}(t) \tag{3.22}$$

where

$$H = \frac{1}{1 + w\omega} \tag{3.23}$$

$$\tilde{H} = \frac{1}{1 + (1 + w)\omega} \tag{3.24}$$

Comparing formulae (3.19), (3.20) and (3.23) it can be found that

$$\mu = \gamma(1 + H\omega)^{\frac{1}{\nu}} \tag{3.25}$$

Formulae (3.23) and (3.24) enable us to evaluate the relation

$$\tilde{H} = \tfrac{H}{1+H\omega} \tag{3.25a}$$

In this way the w–parameter has been deleted and replaced by the H–parameter.

If the functions (3.21) and (3.22) are substituted into constitutive equations (2.1) and (2.2), the following equations will be obtained

$$e_{ij}(t) = \frac{s_{ij}(t)}{2G} + \frac{\omega H}{2G} \int_0^t e_{\nu\gamma}(t-u)s_{ij}(u)du \tag{3.26}$$

$$s_{ij}(t) = 2Ge_{ij}(t) - \frac{2G\omega H}{1 + \omega H} \int_0^t e_{\nu\mu}(t-u)e_{ij}(u)du \tag{3.27}$$

In the above equations the w– and H–parameters do not appear separately but as a product $H\omega$. It means that equations (3.26) and (3.27) would be identical to the similar equations written for the fractional function. It is because the relations between the parameters α and β (Eq (3.7a)) and between the parameters μ and γ (Eq (3.25)) are identical.

The conclusion is that this kind of generalization does not give positive results as no new function is created.

Another possibility of the fractional function generalization is to apply the value $\nu > 1$ to the series (3.2) or to the integral form (3.4).

For the series, a complicated analysis (cf [14,15,16]) leads only to negative results which are summarized in Fig.3.

For the integral form, the character of spectrum $f(M)$ (Fig.4) is as desired. It appears, however, that the calculation of the function $\Psi(t)$ based on the known function $\Phi(t)$ is not possible. After some complex transformations the final result is

$$\Psi(t) = \sum \mathrm{res} + \alpha \frac{|\sin(\Pi\nu)|}{\Pi} \int\limits_0^\infty \exp(-\alpha u t) u^\nu [1 + 2u^\nu \cos(\Pi\nu) + u^{2\nu}] \cdot$$

$$\cdot \Big\{ 1 + 2u^\nu \cos(\Pi\nu) + \omega[1 + u^\nu \cos(\Pi\nu)] + \frac{2\omega}{\nu}[u \cos \frac{\Pi}{\nu} + 1] \cdot$$

$$\cdot \frac{1 + 2u^\nu \cos(\Pi\nu) + u^{2\nu}}{1 + 2u \cos(\Pi\nu) + u^2} \Big\}^{-1} \frac{1}{\omega^2 u^{2\nu} \sin(\Pi\nu)} du \qquad (3.28)$$

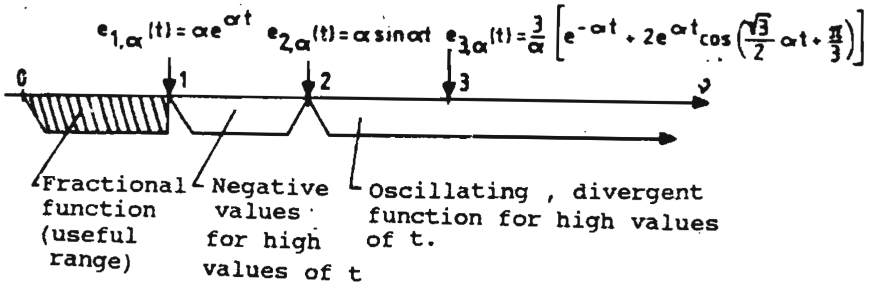

Fig. 3. Applicability of the series representation of the fractional function

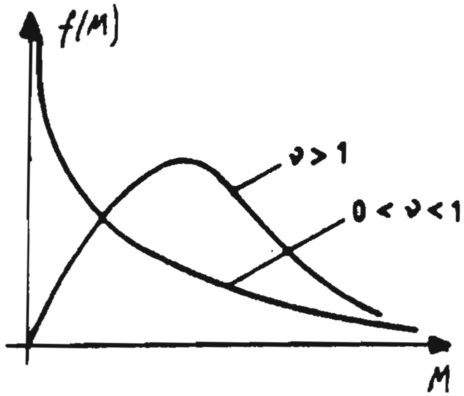

Fig. 4. Plots of molecular weight distribution function $f(M)$ for the fractional function at different ranges of ν

In the given above formula it is not possible to calculate the residua, it does not seem possible to prove that they do not exist either. If the function is written as the strict integral, it will be very difficult for the numerical tabulation because the positive and negative components of the function will mutually delete one another.

Thus the impossibility of recalculating $\Phi(t)$, $\Psi(t)$ makes the result negative.

The next possibility of generalizing the fractional function suggested by Koltunov [18] is to apply the product of the fractional function and the simple exponential function

$$\Phi(t) = e_{\nu\alpha\delta}(t) = \left[1 + \left(\frac{\delta}{\alpha}\right)\right] \exp(-\delta t) e_{\nu\alpha}(t) \tag{3.29}$$

This function fulfills all the listed previously requirements and its Laplace transform is

$$\bar{e}_{\nu\alpha\delta}(p) = \frac{1 + \left(\frac{\delta}{\alpha}\right)^{\nu}}{1 + \left(\frac{p+\delta}{\alpha}\right)^{\nu}} \tag{3.30}$$

The memory function of relaxation written on the base of Eq (2.3) has the form

$$\Psi(t) = \frac{1}{1+\omega} e_{\nu\beta\delta}(t) \tag{3.31}$$

where

$$\beta = \alpha\left[1 + \omega\left(1 + \left(\frac{\delta}{\alpha}\right)^{\nu}\right)\right]^{\frac{1}{\nu}}$$

The newly obtained function can be rewritten in the form

$$e_{\nu\alpha\delta}(t) = \left[1 + \left(\frac{\delta}{\alpha}\right)^{\nu}\right] \alpha \frac{\sin(\Pi\nu)}{\Pi} \int_0^{\infty} \exp[-(\alpha u + \delta)t] \cdot$$

$$\cdot \frac{u^{\nu}}{1 + 2u^{\nu}\cos(\Pi\nu) + u^{2\nu}} du \tag{3.32}$$

$$e^{*}_{\nu\alpha\delta}(t) = \int_0^{t} e_{\nu\alpha\delta}(v) dv = 1 - \left[1 + \left(\frac{\delta}{\alpha}\right)^{\nu}\right] \alpha \frac{\sin(\Pi\nu)}{\Pi} \cdot$$

$$\cdot \int_0^{\infty} \exp[-(\alpha u + \delta)t] \frac{u^{\nu}}{(\alpha u + \delta)(1 + 2u^{\nu}\cos(\Pi\nu) + u^{2\nu})} du \tag{3.33}$$

The spectral functions are expressed by the formulae

$$\Lambda(s) = \left[1 + \left(\frac{\delta}{\alpha}\right)^{\nu}\right] \frac{\sin(\Pi\nu)}{\Pi s} \frac{\left(\frac{s-\delta}{\alpha}\right)^{\nu}}{1 + 2\left(\frac{s-\delta}{\alpha}\right)^{\nu}\cos(\Pi\nu) + \left(\frac{s-\delta}{\alpha}\right)^{2\nu}} \tag{3.34}$$

$$\Pi(s) = \left[1 + \left(\frac{\delta}{\beta}\right)^{\nu}\right] \frac{\sin(\Pi\nu)}{\Pi s(1+\omega)} \frac{\left(\frac{s-\delta}{\beta}\right)^{\nu}}{1 + 2\left(\frac{s-\delta}{\beta}\right)^{\nu}\cos(\Pi\nu) + \left(\frac{s-\delta}{\beta}\right)^{2\nu}} \tag{3.35}$$

If we apply formula (2.11), the spectrum $f(M)$ will have the form

$$f(M) = \left[1 + \left(\frac{\delta}{\alpha}\right)^{\nu}\right] \frac{\sin(\Pi\nu)}{\Pi M^{k}} \frac{\left(\frac{1/M^{k}-\delta}{\alpha}\right)^{\nu}}{1 + 2\left(\frac{1/M^{k}-\delta}{\alpha}\right)^{\nu}\cos(\Pi\nu) + \left(\frac{1/M^{k}-\delta}{\alpha}\right)^{2\nu}} \tag{3.36}$$

The plot of the spectrum will be monotonically decreasing from infinity for $M = 0$ to zero for $M = 1/\delta$ (Fig.5).

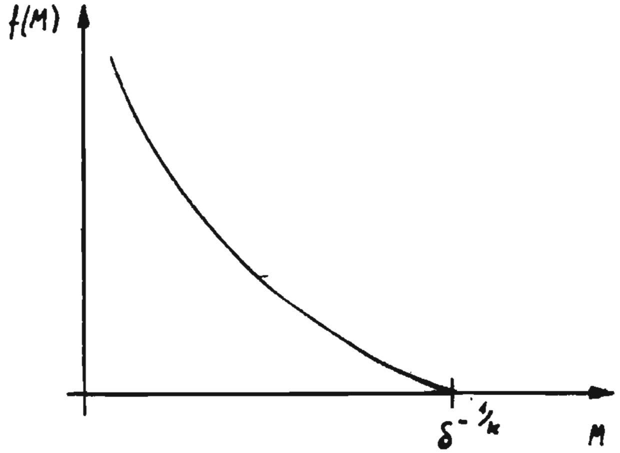

Fig. 5. Plot of molecular weight distribution function $f(M)$ for the Koltunov function $e_{\nu\alpha\delta}(t)$

In conclusion, this function also does not fulfill the requirement concerning its plot. As the application of this function seems to be unuseful, the derived formulae which describe the components of the complex modulus and compliance will not be presented.

Several other functions suggested in the literature (cf [17,18,19,20]) have been analyzed. One of the interesting function is the Williams–Watt fractional function

$$e(t) = \exp\left[-(\alpha t)^{\nu}\right] \tag{3.37}$$

where $0 < \nu < 1$.

The obtained results are negative, mainly due to the impossibility of recalculation of the memory functions $\Phi(t)$, $\Psi(t)$.

3.3. Root function

As a result of a thorough investigation, a new function has been found.
This function is represented by the formula

$$e_{AB}(t) = \frac{AB}{\Pi} \int_{0}^{\infty} \exp(-ut)\, \frac{u^{\frac{3}{2}}}{(Bu-1)^2 + A^2 u} du \tag{3.38}$$

and its Laplace transform is

$$\bar{e}_{AB}(p) = \frac{1 + Ap^{\frac{1}{2}}}{1 + Ap^{\frac{1}{2}} + Bp} \tag{3.39}$$

The memory function of relaxation can be presented as

$$\Psi(t) = \frac{1}{1 + \omega} e_{AC}(t) \tag{3.40}$$

where $C = \frac{B}{1+\omega}$.

It can be seen that this function converts into the exponential function for $A = 0$ (see Eq (3.39)).

The integral of this function has the form

$$e^{*}_{AB}(t) = 1 - \frac{AB}{\Pi} \int_{0}^{\infty} \exp(-ut) \frac{u^{\frac{1}{2}}}{(Bu-1)^2 + A^2 u} du \tag{3.41}$$

Due to the exponent (1/2) which is a characteristic feature of the Laplace transform (Eq (3.39)), this function has been called "root function".

The root function as well as its integral can be transformed into the form more convenient for numerical tabulation

$$e_{A_1B}(t) = \frac{A_1 \alpha}{\Pi} \int_{0}^{\infty} \exp(-\alpha ut) \frac{u^{\frac{3}{2}}}{(u-1)^2 + A_1^2 u} du \tag{3.42}$$

$$e^{*}_{A_1B}(t) = 1 - \frac{A_1}{\Pi} \int_{0}^{\infty} \exp(-\alpha ut) \frac{u^{\frac{1}{2}}}{(u-1)^2 + A_1^2 u} du \tag{3.43}$$

where

$$A_1 = AB^{-\frac{1}{2}} \qquad \alpha = \frac{1}{B}$$

The memory function of relaxation can be transformed in an analogous way as previously presented memory function of creep. It can be expressed by the formula

$$\Psi(t) = \frac{1}{1 + \omega} e_{A_2\gamma}(t) \tag{3.44}$$

where

$$A_2 = A_1(1 + \omega)^{\frac{1}{2}} \qquad \gamma = \alpha(1 + \omega)$$

The plots of the root function as well as of its integral are presented in Fig.6 and Fig.7.

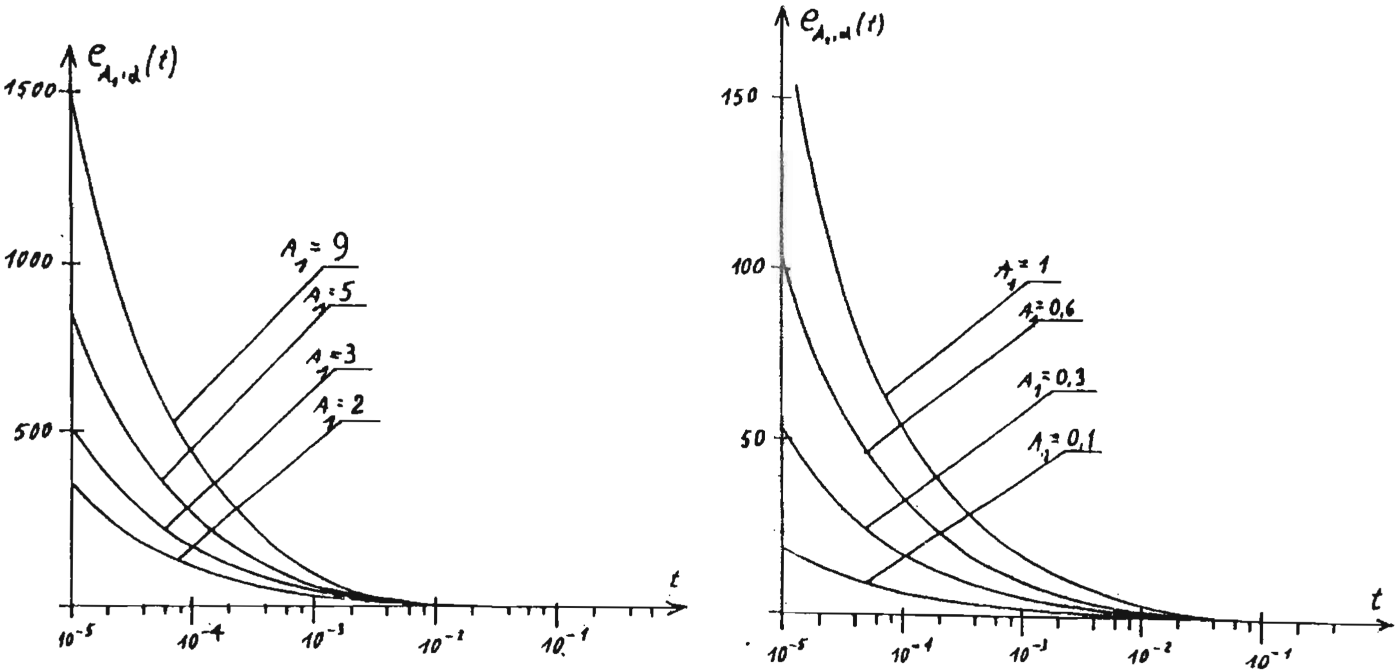

Fig. 6. Plots of root function $e_{A_1\alpha}(t)$ for $\alpha = 1$

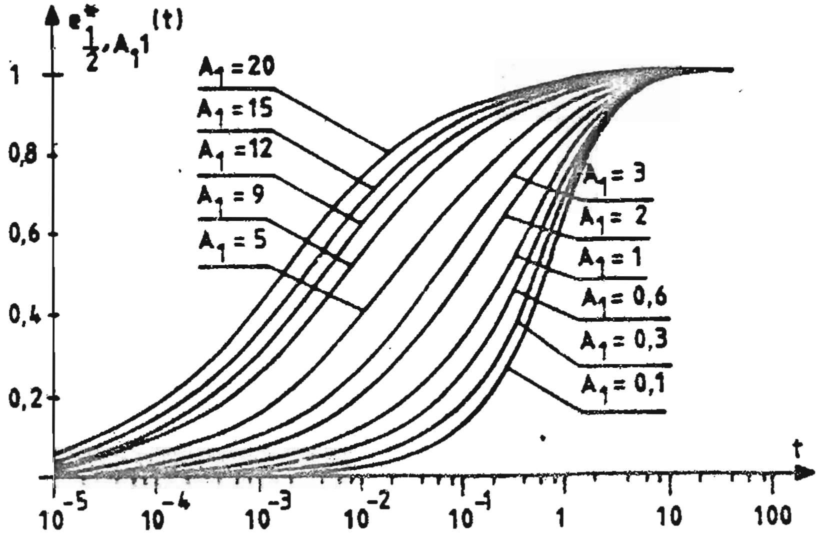

Fig. 7. Plots of the integral of the root function $e^*_{A_1\alpha}(t)$

The components of the complex modulus and the complex compliance can be written as follows

$$J'(n) = \frac{1}{2G}\left[1 + \omega \frac{1 + A_1^2\frac{n}{\alpha} + \frac{3}{2}A_1\left(\frac{2n}{\alpha}\right)^{\frac{1}{2}}}{1 + A_1^2\frac{n}{\alpha} + \left(\frac{n}{\alpha}\right)^2 + A_1\left(\frac{2n}{\alpha}\right)^{\frac{1}{2}} - A_1\frac{n}{\alpha}\left(\frac{2n}{\alpha}\right)^{\frac{1}{2}}}\right] \tag{3.45}$$

$$J''(n) = \frac{\omega}{2G} \frac{\frac{A_1}{2}\left(\frac{2n}{\alpha}\right)^{\frac{1}{2}} - \frac{n}{\alpha}}{1 + A_1^2\frac{n}{\alpha} + \left(\frac{n}{\alpha}\right)^2 + A_1\left(\frac{2n}{\alpha}\right)^{\frac{1}{2}} - A_1\frac{n}{\alpha}\left(\frac{2n}{\alpha}\right)^{\frac{1}{2}}} \tag{3.46}$$

$$G'(n) = 2G\left[1 - \frac{\omega}{1+\omega} \frac{1 + A_2^2\frac{n}{\gamma} + \frac{3}{2}A_2\left(\frac{2n}{\gamma}\right)^{\frac{1}{2}}}{1 + A_2^2\frac{n}{\gamma} + \left(\frac{n}{\gamma}\right)^2 + A_2\left(\frac{2n}{\gamma}\right)^{\frac{1}{2}} - A_2\frac{n}{\gamma}\left(\frac{2n}{\gamma}\right)^{\frac{1}{2}}}\right] \tag{3.47}$$

$$G''(n) = \frac{2G\omega}{1+\omega} \frac{\frac{A_2}{2}\left(\frac{2n}{\gamma}\right)^{\frac{1}{2}} - \frac{n}{\gamma}}{1 + A_2\frac{n}{\gamma} + \left(\frac{n}{\gamma}\right)^2 + A_2\left(\frac{2n}{\gamma}\right)^{\frac{1}{2}} - A_2\frac{n}{\gamma}\left(\frac{2n}{\gamma}\right)^{\frac{1}{2}}} \tag{3.48}$$

It is possible to calculate the distribution functions as

$$A(s) = \frac{A_1}{\Pi\alpha} \frac{\left(\frac{s}{\alpha}\right)^{\frac{1}{2}}}{\left(\frac{s}{\alpha} - 1\right)^2 + A_1^2\frac{s}{\alpha}} \tag{3.49}$$

$$\Pi(s) = \frac{A_2}{\Pi\gamma(1+\omega)} \frac{\left(\frac{s}{\gamma}\right)^{\frac{1}{2}}}{\left(\frac{s}{\gamma}-1\right)^2 + A_2^2\frac{s}{\gamma}} \tag{3.50}$$

The MWD function can be rewritten basing on formulae (2.8) and (2.11) and it will be

$$f(M) = \frac{A_1}{\Pi\alpha} \frac{\left(\frac{1}{\alpha M^k}\right)^{\frac{1}{2}}}{\left(\frac{1}{\alpha M^k}-1\right)^2 + \frac{A_1^2}{\alpha M^k}} \frac{1}{M^{2k}} \tag{3.51}$$

The asymptotics of the function $f(M)$ are the same as for the fractional function i.e. the plot is monotonically decreasing from infinity to zero for $M \in (0,\infty)$ for $k > 0$. Such character of plot does not meet the previous requirements. If we consider, however, a function defined by Eq (2.11) but with the factor $1/M^{2k}$ truncated, the function $\tilde{f}(M)$ obtained in such a way called incomplete MWD function will have the form

$$\tilde{f}(M) = \frac{A_1}{\Pi\alpha} \frac{\left(\frac{1}{\alpha M^k}\right)^{\frac{1}{2}}}{\left(\frac{1}{\alpha M^k}-1\right)^2 + \frac{A_1^2}{\alpha M^k}} \tag{3.52}$$

It has the asymptotics

$$\lim_{M\to 0} \tilde{f}(M) = 0 \qquad \lim_{M\to\infty} \tilde{f}(M) = 0$$

for each $k > 0$.

Thus the plot of the incomplete MWD–function will be in accordance with the requirements.

The integral of the incomplete MWD–function will be convergent to a finite value

$$\int_0^\infty f(M)dM < \infty \tag{3.53}$$

for each $k > 2$.

It can be concluded that in the case of the root function it is possible to separate the incomplete MWD–function $\tilde{f}(M)$ which can be directly compared with the MWD curve obtained from traditional GPC (Gel Permeation Chromatography) methods. Such a comparison will be presented in the next chapter.

4. Experimental

4.1. A complex program of deformation

In order to verify experimentally the described function, a complex rheological program of deformation has been applied. The experimental curves of stress and strain vs. time were compared with the numerical simulation based on the applied memory functions.

The selected material underwent the following rheological process

— deformation at a constant strain-rate $\dot{\varepsilon}$

— creep at a constant stress σ

— relaxation at a constant strain ε

— relief at a constant strain - rate $\dot{\varepsilon}$

— recovery at the stress equal zero.

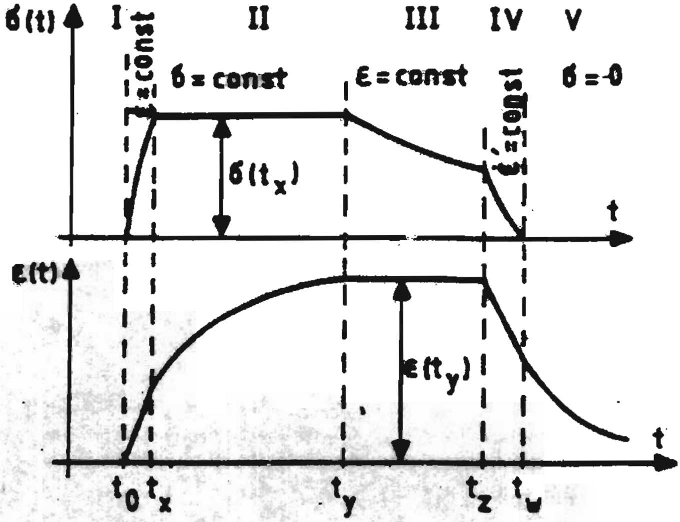

Fig. 8. Complex, five-steps program of deformation

The first two steps were utilized for the evaluation of the parameters of the constitutive equation; the next ones – to verify the obtained results.

This method enables us to eliminate the fluctuation of the properties of the material from one sample to another because only one sample can be used both to evaluate the parameters and to verify their values.

The constitutive equations described each of the five steps of the rheological process.

The material underwent uniaxial stretching; that is why the symbols used differ from those in Eqs (2.1) and (2.2).

It was assumed that both deviatoric and hydrostatic components of the strain tensor were described by the same function. This simplification seems to be acceptable.

Finally the five steps will be described by the following equations

— first step – deformation at a constant strain–rate $\dot{\varepsilon}$

$t \in [t_0, t_x]$, $\varepsilon(t) = \dot{\varepsilon}t$

$$\sigma(t) = E\dot{\varepsilon}t - E\omega\dot{\varepsilon}\int\limits_0^t \Psi(t-u)u\,du \tag{4.1}$$

— second step – creep at a constant stress σ

$t \in [t_x, t_y]$, $\sigma(t) = \sigma(t_x) =$const

$$\varepsilon(t) = \frac{\sigma(t_x)}{E} + \frac{\omega}{E}\int\limits_0^{t_x} \Phi(t-u)\underline{\sigma(u)}du + \omega\frac{\sigma(t_x)}{E}\int\limits_{t_x}^{t} \Phi(t-u)du \tag{4.2}$$

where $\underline{\sigma(u)}$ should be calculated in the first step;

— third step – relaxation at a constant strain ε

$t \in [t_y, t_z]$, $\varepsilon(t) = \varepsilon(t_y) =$ const

$$\begin{aligned}\sigma(t) &= E\varepsilon(t_y) - E\omega\dot{\varepsilon}\int\limits_{t_0}^{t_x} \Psi(t-u)u\,du - \\ &- E\omega\int\limits_{t_x}^{t_y} \Psi(t-u)\underline{\varepsilon(u)}du - E\omega\varepsilon(t_y)\int\limits_{t_y}^{t} \Psi(t-u)du\end{aligned} \tag{4.3}$$

where $\underline{\varepsilon(u)}$ should be calculated in the second step;

— fourth step – relief at a constant strain–rate $\dot{\varepsilon}'$

$t \in [t_z, t_w]$, $\varepsilon(t) = \varepsilon(t_z) + \dot{\varepsilon}' \cdot (t - t_z)$

$$\begin{aligned}\sigma(t) &= E[\varepsilon(t_z) + \dot{\varepsilon}' \cdot (t-t_z)] - E\omega\dot{\varepsilon}\int\limits_{t_0}^{t_x} \Psi(t-u)u\,du - \\ &- E\omega\int\limits_{t_x}^{t_y} \Psi(t-u)\underline{\varepsilon(u)}du - E\omega\varepsilon(t_z)\int\limits_{t_y}^{t_z} \Psi(t-u)du - \\ &- E\omega\int\limits_{t_z}^{t} \Psi(t-u)[\varepsilon(t_z) + \dot{\varepsilon}' \cdot (u-t_z)]du\end{aligned} \tag{4.4}$$

where $\underline{\varepsilon(u)}$ should be calculated in the second step;

— fifth step – recovery at the stress equal zero
$t > t_w, \quad \sigma(t) = \sigma(t_w) = \text{const}$

$$\varepsilon(t) = \frac{\sigma(t_w)}{E} + \frac{\omega}{E}\int_{t_0}^{t_x} \Phi(t-u)\underline{\sigma(u)}du + \frac{\omega\sigma(t_x)}{E}\int_{t_x}^{t_y} \Phi(t-u)du + \tag{4.5}$$

$$+\frac{\omega}{E}\int_{t_y}^{t_z} \Phi(t-u)\underline{\sigma(u)}du + \frac{\omega}{E}\int_{t_z}^{t_w} \Phi(t-u)\underline{\sigma(u)}du + \frac{\omega\sigma(t_w)}{E}\int_{t_w}^{t} \Phi(t-u)du$$

where $\underline{\sigma(u)}$ should be calculated in the first, third and fourth steps respectively.

4.2. Material tested and the testing device

The experiments were performed on polycarbonate "Lexan" (Du Pont – USA). Paddle – shaped samples were cut mechanically from the injected plate of the 6 mm thickness. Cross section of the samples was 8 × 6 mm, the gauge–length – 55 mm. The samples were stored for 10 days in the vicinity of the tester and then heated for 24 hours in the heating chamber before the experiment started. The presented results are average values from 5 different tests. All tests were run on an originally designed tester which was described in detail earlier (cf [21]).

4.3. Discussion of the results

In order to obtain the best curve fitting for the first and the second step of the process, the least squares method was used.

The calculated parameters for the tested polycarbonate are presented in the following table

Material			root function				fractional f.		
	E	ω	A_1	α	A_2	γ	ν	α	β
	[MPa/%]	[1]	[1]	[1/h]	[1]	[1/h]	[1]	[1/h]	[1/h]
PC	11.99	0.73	40	$6 \cdot e^{-5}$	52	$104 \cdot e^{-6}$	0.5	$88 \cdot e^{-3}$	0.263

The plots of the process as well as the simulation with the help of the fractional and the root functions are presented in Fig.9. It can be seen that both functions are suitable to simulate the process. It is confirmed by the least square delta Δ

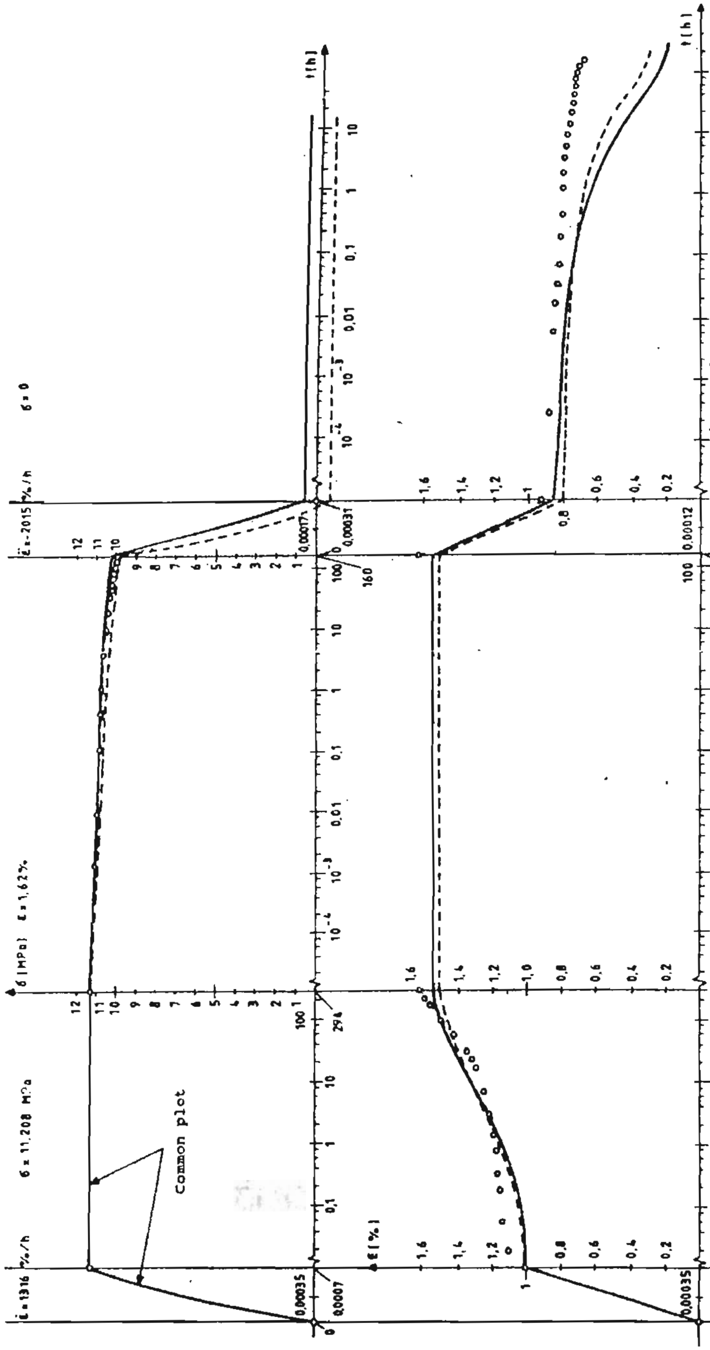

Fig. 9. Experimental results (points) and simulation of the process with the help of the root function (continous line) and the fractional function (broken line) for polycarbonate "Lexan" at 368 K

which was defined as

$$\Delta = \sum_{i=1}^{n} (\varepsilon_{i\ \mathrm{exp}} - \varepsilon_{i\ \mathrm{calc}})^2 \tag{4.6}$$

The values of Δ calculated in the first and the second steps should be as small as possible and create the criterion of the curve fitting. Their values are: $\Delta = 0.109$ for the fractional function and $\Delta = 0.061$ for the root function respectively. It is interesting to compare the simulation of the process with the help of the two described functions to the simulation in terms of the double exponential function (cf [6]). It can be seen (cf [6]) that the double exponential function gives a better result ($\Delta = 0.0102$). This result is unexpected; it should not be, however, concluded that the double exponential function simulates better the phenomena of viscoelasticity. The complexity of the mathematical description (Eqs.(4.1) $\div$ (4.5)) and the resulting possible numerical errors are more likely to be the reason. We should note that the exponential function enables us to use the ready analytical solutions.

Another reason may arise from the fact that in a viscoelastic material during uniaxial stretching test both the deviatoric and the hydrostatic components of the strain tensor occur. Consequently, the basically better (but single) functions used in this paper may give worse simulation than a very simple double exponential function.

The interesting thing is a very good convergence of the MWD–curve obtained from the traditional GPC method and the curve calculated from the presented rheological tests (Fig.10).

It should be noted that the function $\tilde{f}(M)$ which represents the relation between the molecular weight distribution and the distribution of the time constants is formally not proper and may have only a qualitative application. Even though this disadvantage occurs, the convergence of the curves is very good. The conclusion is that searching for new memory function which permits for this kind of correlation should be continued. It seems that the fractional function represented by the integral for $\nu > 1$ has rather good prospects. The difficulties concerning the mutual recalculation of the memory functions could be solved numerically. The methods used in creating the root function (Eq (3.39)) could probably be utilized in working out new formulae. It should also be stressed that the possibility of determination of molecular weight distribution based on a rheological test is of an important practical use.

The traditional gel permeation chromatography method can be applied only to soluble plastics as it tests different concentrations of solutions. This is why the worldwide chemical companies focus their attention on the rheological methods.

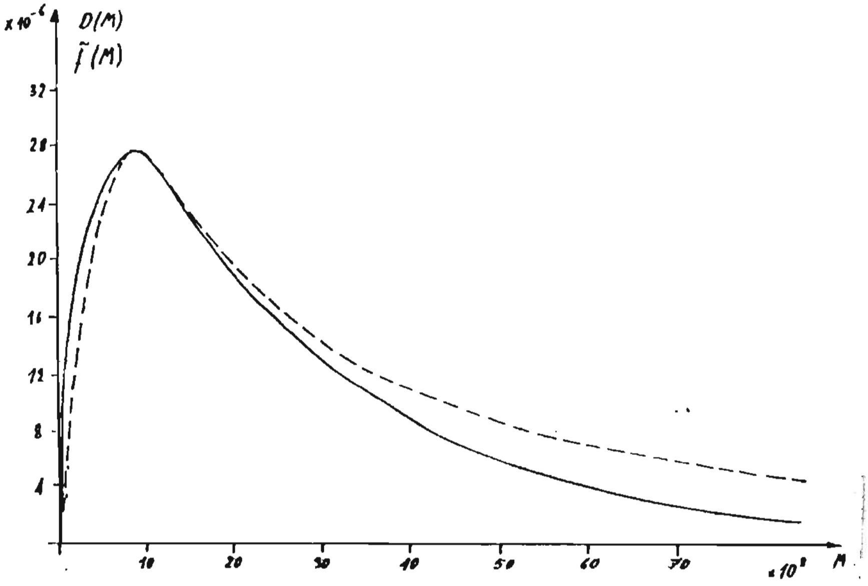

Fig. 10. Comparison of the MWD–curve (continous line) for the polycarbonate "Lexan" and the function $f(M)$ (broken line) calculated from rheological tests

5. Conclusions

1. Two of the analyzed functions used as memory functions in the constitutive equations of viscoelasticity are suitable for the simulation of the material behaviour. They are: the fractional function and the root function.

2. The root function introduced in this paper allows for a correlation between the behaviour of the material in macroscale and the structure of the material. The methods used in creating this function could be utilized in working out new, competitive functions.

3. Further developement of the fractional function represented by the integral for $\nu > 1$ may bring interesting results.

4. The significant aspect of this work is the possibility of the molecular weight distribution determination basing on relatively simple rheological tests. This method is competitive and more universal compared with the traditional, chemical methods.

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Zastosowanie wybranych funkcji pamięci do opisu liniowej lepkosprężystości polimerów konstrukcyjnych

Streszczenie

Praca przedstawia możliwości zastosowania funkcji typu wykładniczego do opisu liniowej lepkosprężystości polimerów. Funkcje te spełniają rolę tzw. funkcji pamięci w równaniach konstytutywnych, których istotnym elementem są całki Volterry. Równania te są częścią ogólnej teorii sprężystości, która jest systemem matematycznie spójnym. Umożliwia to wyznaczenie wszystkich funkcji charakteryzujących ciało lepkosprężyste takich jak widma, składowe modułu i podatności zespolonej itp. W pracy tej wprowadzono nową funkcję pamięci konkurencyjną w stosunku do funkcji znanych.

Zaproponowany opis został zweryfikowany przy użyciu złożonego programu badań reologicznych. Wartości liczbowe parametrów równania konstytutywnego wyliczono w oparciu o próbę pełzania. Weryfikacja polegała na zastosowaniu odmiennego rodzaju badania i na porównaniu otrzymanych w ten sposób wyników z symulacją numeryczną wykonana, przy zastosowaniu wyliczonych uprzednio parametrów.

Niezależnie od weryfikacji czysto fenomenologicznej, dokonano porównania rozkładu masy cząsteczkowej z krzywą wyznaczoną na podstawie nowo wprowadzonej funkcji pamięci. Dobra zbieżność zarówno krzywych symulujących procesy reologiczne jak i krzywej rozkładu masy cząsteczkowej z wynikami eksperymentalnymi potwierdza właściwy dobór funkcji pamięci.

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