

dedicated to Professor K. Walters on his seventieth Birthday

CONTINUOUS RELAXATION SPECTRUM – ITS ADVANTAGES AND METHODS OF CALCULATION

A.Ya. MALKIN*

Institute of Petrochemical Synthesis,
Russian Academy of Sciences,
Moscow, Russia
e-mail: alex_malkin@mig.phys.msu.ru

Some advantages in treating experimental data on viscoelastic properties of polymeric materials in terms of a continuous spectrum instead of generally used fitting these data by means of a discrete relaxation times spectrum were demonstrated. The proposed continuous spectrum of a power-like type contains only three adjustable parameters. They can be found from integral characteristics of viscoelastic material, such as instantaneous modulus, Newtonian viscosity, areas under shear and normal stress relaxation curves. The proposed continuous spectrum correctly reflects main peculiarities of viscoelastic properties of real polymeric materials in a wide frequency range.

Key words: relaxation spectrum, rheology, viscoelasticity, polymer melts, inverse problems.

1. Introduction

The theory of viscoelasticity the problem of relaxation spectrum calculation. Though this conception is formulated in the frames of the linear theory of viscoelasticity, it has the fundamental meaning for describing the non-linear behavior of viscoelastic materials as well as the necessary limiting case. Theoretical interest in calculating a relaxation spectrum is based on a supposition that it reflects molecular movements of macromolecules and thus can be connected with the molecular structure (molecular mass and molecular mass distribution, branching and other details of molecular architecture). From the practical point of view the knowledge of a relaxation spectrum allows one to find stress-vs.-deformation relationships in any arbitrary deformation mode.

Meanwhile the principle point is that it is impossible to *measure* a relaxation spectrum, it can be only *calculated* on the basis of experimental data (frequency dependencies of dynamic functions, creep or relaxation functions or others). The main difficulty of this problem is that this function is introduced as a formal conception (see, e.g. Gross, 1953; Tschoegl, 1989 and Malkin, 2002) and its determination is based on the solution of the ill posed inverse problem (Honerkamp, 1989 and Malkin, 1990).

If not to come back to earlier pre-computer era methods of relaxation spectrum calculations (one can find them in the classical monograph by Ferry, 1980), today's methods are based on the computer-aided minimization of the functional of errors in approximation of experimental data with some set of separate relaxation modes (lines in a discrete spectrum).

The formal approach to solving ill-posed problems is based on the regularization procedure as was proposed and used by Honerkamp and Weese (1989), Elser *et al.* (1992). However, other methods have also been discussed in the literature.

So, the method of direct calculation of constants (relaxation times and their weights) by a non-linear fitting procedure (so called IRIS method) was proposed by Baumgärtel and Winter (1989), Jackson *et al.* (1994), and later widely used by many authors including its usage in the software of industrial rheometers. This method was thoroughly analyzed by Winter (1997). He supposes that the "simultaneous inversion of two interrelated integrals" (for storage and loss moduli) for a relaxation spectrum calculation excludes the ill-

* To whom correspondence should be addressed

posedness of the problem under discussion. This statement was not strictly proven and other methods discussed in the literature give different predictions concerning the time distribution in a relaxation spectrum.

The main problem in fitting experimental data (for example frequency dependence of storage modules in a wide frequency range) by a relaxation time spectrum is the non-linearity of the fitting procedure that presumes the ambiguity of the results of calculation. In order to avoid this difficulty it is reasonable to pass to semi-inverse procedure of calculations. It can be realized by the initial rigid fixing of relaxation times distribution. Then only their weights should be found, the distribution might be equidistant in a logarithmic scale (Emri and Tschoegl, 1993 and Tschoegl and Emri, 1993) or any other. Also, a linearization procedure for the search of parameters of a relaxation spectrum has been proposed (Malkin and Kuznetsov, 2000) that makes the results of calculations unambiguous.

It is important to stress that different methods of a relaxation spectrum calculation give non-coinciding results. The comparison and analysis of correlation of the results obtained with the application of different fitting procedures has been made by Malkin and Masalova (2001). It was shown that different approaches give the set of relaxation times lying inside a rather narrow band, though being not equivalent. Then the usage of different calculated spectra is practically equivalent in predictions of mechanical behavior of viscoelastic liquids. This result is in line with the general belief that the choice of the algorithm in a relaxation spectrum calculation is the problem of “personal preference rather than objective definition” (Winter, 1997) and “no line spectrum – produced by whatever method – is ever the true spectrum” (Emri and Tschoegl, 1993).

However, in the paper of Malkin and Masalova (2001) it was mentioned that different procedures, presenting the same results in predicting visco-elastic behavior of a polymer melt “in average”, give non-equivalent figures for those integral characteristics of visco-elastic behavior, for which the boundary values of relaxation times are the most important, that is instantaneous modules and the coefficient of normal stresses. This is a natural consequence of ambiguity in calculated relaxation spectra and due to freedom in the choice of boundaries. Meanwhile, the rigid fixation of the boundaries is impossible in the frames of discrete spectrum approximation.

Sometimes the attempts to pass to continuous spectra were carried out (Baumgärtel and Winter, 1992 and Jackson *et al.*, 1994). However, this approach was not formulated in the terms allowing one to calculate a spectrum basing on a limited set of experimental data.

In this paper, the attempt to introduce the concept of a continuous spectrum as having several definite advantages in comparison with standard fitting experimental data with discrete spectra is made. There are at least two serious advantages – very limited number of free constants that allows one to use very limited number of experimental data, and a possibility for an easy correlation of such spectra with integral characteristics of visco-elastic behavior of a material. The latter is the base for this study.

2. Results and discussion

Two points mentioned above are the grounds for further discussion. First, a similarity (though not equivalency) of relaxation time distributions along the time axis obtained by different methods was observed. Second, wrong predictions for experimental values of the integral characteristics of a relaxation spectrum strongly dependent on boundary values of relaxation times in a spectrum were found.

The first statement is illustrated in Fig.1, which collects data from the paper of Malkin and Masalova (2001). The position of the calculated points prompts that it is reasonable to find a continuous spectrum in the power-type form as shown by the straight line drawn in this figure additionally to experimental points. This line is not the “average” for all experimental points because the points obtained by different fitting procedures cannot be fitted by a single dependence but only hint that a spectrum of such forms might be applicable for any set of calculated points.

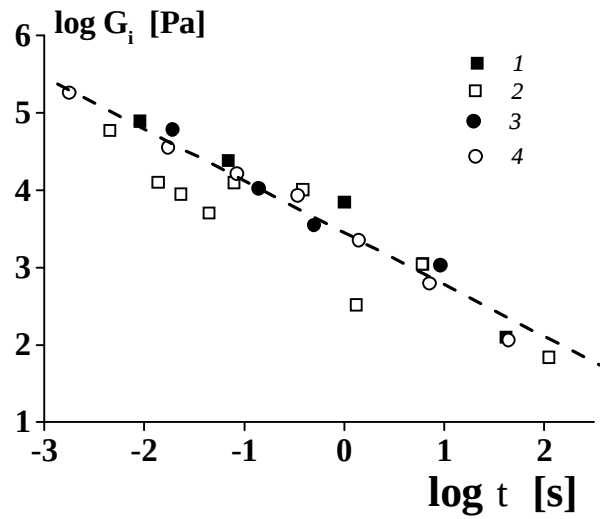


Fig.1. Discrete relaxation spectra as calculated from the same experimental data by different fitting procedure: 1 – equidistant time distribution; 2 – distribution by power law; 3 – linearization procedure; 4 – non-linear minimization of functional of errors.

So, a relaxation time spectrum being discrete presumably looks like

$$G(t) = \sum_{n=0}^N K_n \tau^{-\beta} \delta(\tau - \tau_n) \quad (2.1)$$

where τ_n and K_n are relaxation time values and their weights, respectively, N is the number of lines in a relaxation spectrum, β is a characteristic parameter and δ is delta-function which is equal to 1 at the points $\tau = \tau_n$ and is zero at all other points.

Besides the following relationship describing the time distribution along the time axis is valid

$$\tau_n = \tau_{max} \Delta^{-n} \quad (2.2)$$

where τ_{max} is the maximal value (boundary) of the time distribution and Δ is the step in the distribution.

This power-type discrete spectrum, when transits into a continuous spectrum, is described by a formula

$$G(\tau) = K_0 \tau^{-\alpha}, \quad (2.3)$$

and this spectrum exists from zero till τ_{max} .

It is necessary to mention that presentations of relaxation properties of viscoelastic materials in the form analogous to Eq.(2.3) can be found in some publications (see e.g. Winter, 1997) though the complete subsequent analysis of this form of a relaxation spectrum was absent.

So, there are three characteristic constants describing a continuous relaxation spectrum: K_0 , α and τ_{max} .

In order to find these constants it is necessary to have three representative experimental data. It is supposed that these experimental points are the moments of a relaxation spectrum, which have definite physical meaning (see e.g. Vinogradov and Malkin, 1980):

The zeroth-moment is an instantaneous module

$$G_0 = \int_0^{\tau_{max}} K_0 \tau^{-\alpha} d\tau = \frac{1}{1-\alpha} K_0 \tau_{max}^{1-\alpha}. \quad (2.4)$$

This is also the high-frequency limit of the storage-vs.-frequency dependence.

The first moment is Newtonian viscosity

$$\eta_0 = \int_0^{\tau_{max}} K_0 \tau^{1-\alpha} d\tau = \frac{1}{2-\alpha} K_0 \tau_{max}^{2-\alpha}. \quad (2.5)$$

The second moment is the initial coefficient of the first difference of normal stresses

$$\zeta_0 = \int_0^{\tau_{max}} K_0 \tau^{2-\alpha} d\tau = \frac{1}{3-\alpha} K_0 \tau_{max}^{3-\alpha}. \quad (2.6)$$

So, there are three experimentally defined constants, G_0 , η_0 and ζ_0 .

It would seem enough to find three characteristic constants determining a relaxation spectrum. However, the instantaneous module is rather hardly measured value in regular experiments. Therefore it is reasonable to introduce into discussion the third moment of a relaxation spectrum – a value, which to the best of our knowledge is not considered in rheological literature. Meanwhile this value is also easily measured in regular experiments.

For this purpose let us consider the process of relaxation of normal stresses after cessation of steady flow. This process is described (Malkin, 1968) as

$$\frac{N_1^-}{2\psi^2} = \int_0^{\infty} \tau^2 G(\tau) e^{-t/\tau} \left(1 + \frac{t}{\tau}\right) d\tau, \quad (2.7)$$

and the area, S_N under the normal stress relaxation curve equals

$$S_N = 2\psi^2 \int_0^{\infty} \int_0^{\infty} \tau^2 G(\tau) e^{-t/\tau} \left(1 + \frac{t}{\tau}\right) dt d\tau = 4\psi^2 \int_0^{\infty} \tau^3 G(\tau) d\tau = \frac{4}{4-\alpha} K_0 \tau_{max}^{4-\alpha}. \quad (2.8)$$

It is also interesting to mention that the area under shear stress relaxation curve, S_τ , is equal to the second moment of a relaxation spectrum. So the $\tau(t)$ measurements can be used instead of ζ_0 according to Eq.(6).

So, any three of rather easily measured rheological characteristics of a material, G_0 , η_0 , ζ_0 , S_τ and S_N , can be used for the determination of a relaxation spectrum.

The above written formulas can be slightly rearranged in order to make the search for parameters of a relaxation spectrum easier. So, combining Eqs (2.5), (2.6) and (2.8) it is possible to receive the formula for the experimentally found dimensionless factor X determined by only one parameter of a spectrum α

$$X \equiv \frac{\eta_0 S_N}{\zeta_0^2} = \frac{4(3-\alpha)^2}{(4-\alpha)(2-\alpha)}. \quad (2.9)$$

The dependence of X on the right side of Eq.(9) is shown in Fig.2.

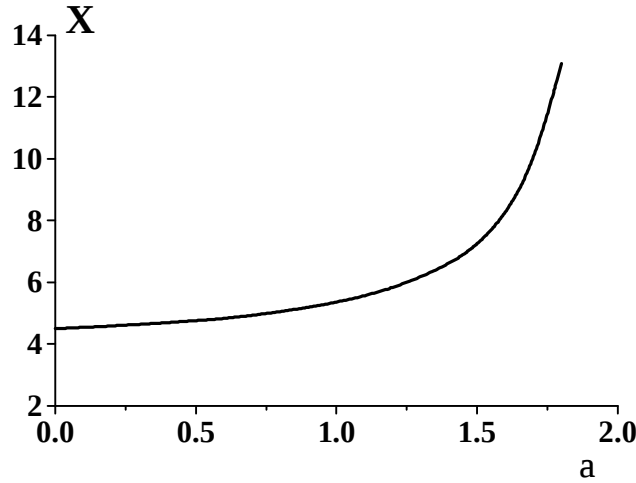


Fig.2. The relationship between the experimentally found dimensionless factor X and characteristic parameter of a relaxation spectrum α .

Then, measuring the complex X it is easy to find the characteristic parameter α .

Then maximal relaxation time, a very important characteristic parameter used in various applications for comparing polymers with different molecular masses can be found from Eqs (2.5) and (2.6) as

$$\tau_{max} = \frac{3 - \alpha \zeta_0}{2 - \alpha \eta_0}. \quad (2.10)$$

Now it is rather interesting to follow the predictions of the spectrum presented in Eq.(2.3) by varying its characteristic parameter values. In this case the direct problem is considered: calculation of frequency dependencies of the component of dynamic modules, $G'(\omega)$ and $G''(\omega)$, using the standard equations

$$G'(\omega) = \int_0^{\tau_{max}} G(\omega) \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} d\tau; \quad G''(\omega) = \int_0^{\tau_{max}} G(\omega) \frac{(\omega\tau)}{1 + (\omega\tau)^2} d\tau. \quad (2.11)$$

Figure 3 demonstrates the results of calculations at the fixed value of τ_{max} and varying values of the slope α . The results are very typical for viscoelastic properties and it is seen that the change in relative position of the dependencies $G'(\omega)$ and $G''(\omega)$ can be really reflected by variation of the parameter α . It can be supposed that, for example, variation of α is connected with changes in molecular weight distribution.

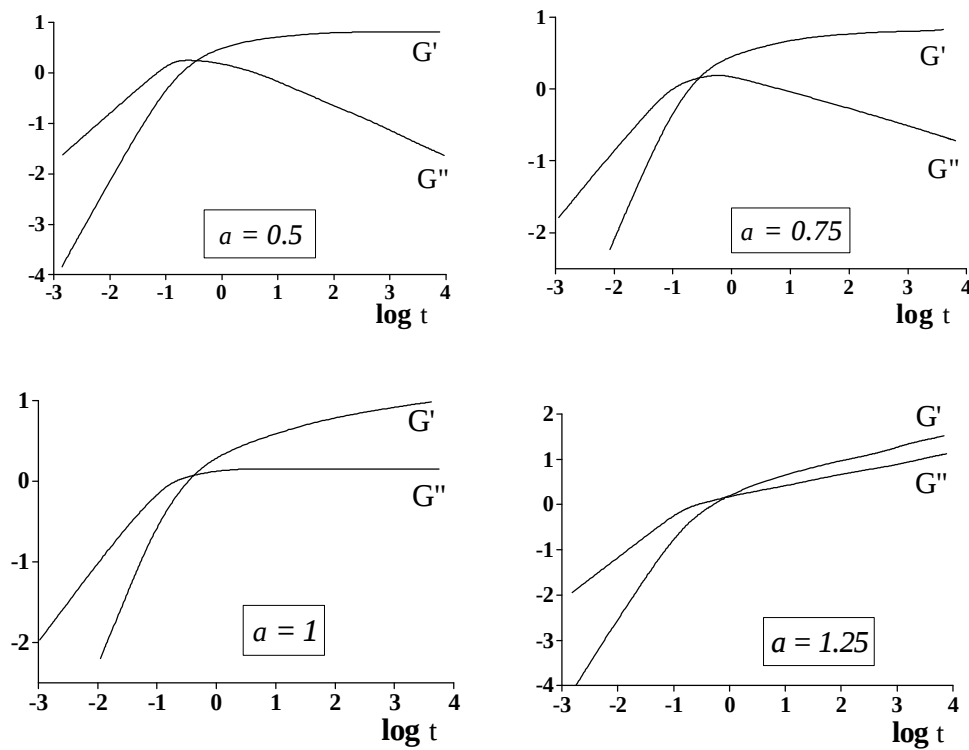


Fig.3. Frequency dependencies of storage and loss modules obtained by varying the parameter α at the same value of $\tau_{max} = 10$.

Another quite illustrative example of the results of predictions made from Eq.3 is shown in Fig.4, which reflects the role of τ_{max} . It is seen that the changing of τ_{max} results in the systematic shift of the $G'(\omega)$ and $G''(\omega)$ dependencies. In the study of polymeric melts, it corresponds to the shift of dynamic modules due to variation of molecular mass. Indeed, it is well known that molecular mass is directly related to maximal relaxation time.

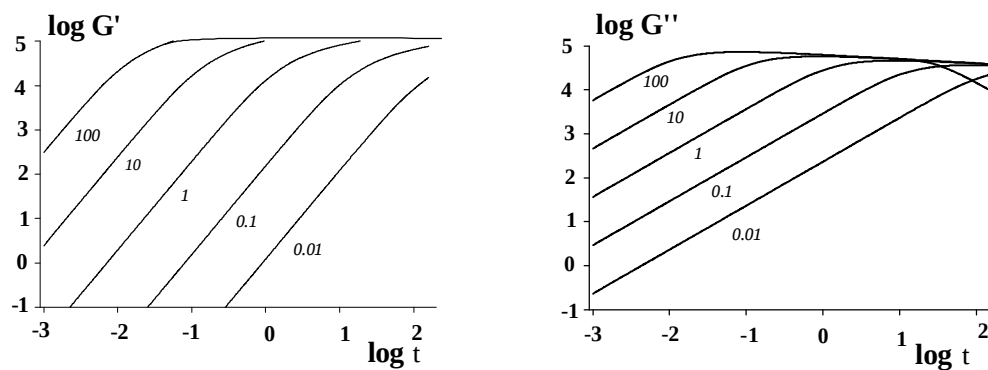


Fig.4. Frequency dependencies of the components of dynamic modules – influence of the maximal relaxation times, τ_{max} (shown at the curves) at constant value of $\alpha = 0.9$.

Figure 5 presents a comparison of experimental data for polypropylene melt (experimental details and original data one can find elsewhere, Malkin and Masalova, 2001) with the curves calculated via Eqs (2.11) with a spectrum described by Eq.3. The values of the parameters of a relaxation spectrum are as follows: $K_0 = 1.5 \times 10^4$, $\alpha = 1.37$, $\tau_{mac} = 58.2 \text{ s}$. One can see that the use of the spectrum in a simple power-like form provides quite satisfactory prediction of experimental data in a wide frequency range (app. 6 decades). However this set of parameters does not predict the existence of the limiting values of modules (instantaneous modules as in Eq.4). This is in line with experimental data of Fig.5, which do not show the existence of plateau and, besides confirms that the third moment of a relaxation spectra should be used instead of instantaneous modules for fitting experimental data (at least if a clearly expressed plateau is absent). In the example presented in Fig.4 plateau exists because in this case $\alpha < 1$.

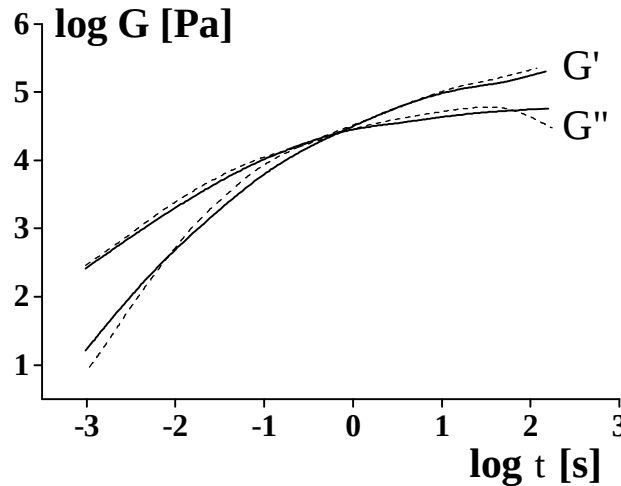


Fig.5. Comparison of experimental data for frequency dependencies of the components of dynamic modules (solid lines) with dependencies calculated basing on Eq.3 (dashed lines) for a polypropylene melt.

The last remark concerns the transition from the linear domain of viscoelastic behavior to a non-linear region. In many experimental works, it was mentioned (see, e.g. Vinogradov and Malkin, 1980) that increasing shear rate leads to the acceleration of a relaxation process. This effect can be treated in terms of truncation of an initial relaxation spectrum from the low-relaxation-time side. This process can be easily described in the terms of a continuous spectrum with monotonous shear-rate-dependent shift of the upper boundary while treating this effect in terms of a discrete spectrum requires jump-like changes in the relaxation behavior that contradicts experimental facts.

Though a power-like relaxation spectrum approximation looks rather promising for treating viscoelastic behavior of polymeric materials, it is definitely not a universal approach. Indeed, according to Eq.3 the curves $G'(\omega)$ and $G''(\omega)$ are expected to cross as in Fig.3, while other experimental data are known with the non-crossing $G'(\omega)$ and $G''(\omega)$ dependencies (e.g. Sohn and Rajagopalan, 2004). Definitely, the latter presents the other type of viscoelastic behavior.

3. Conclusion

It is proposed to treat experimental data on viscoelastic properties of polymeric materials in terms of a continuous spectrum of a power-like type instead of generally used fitting of viscoelastic characteristics by means of the set of discrete relaxation times (lines). The proposed approach has some advantages. It contains only three “free” adjustable parameters, which can be easily found from experimentally measured integral

characteristics of a viscoelastic material, such as instantaneous modules, Newtonian viscosity, areas under shear and normal stress relaxation curves. The model calculations were made on the basis of this spectrum with varying values of its parameters. The predicted frequency dependencies of storage and loss moduli correctly reflect main peculiarities of viscoelastic properties of real polymeric materials, primarily polymer melts. The reliability of the proposed approach was illustrated also by the correspondence of real experimental data obtained for the polypropylene melt and the results of calculations in a wide frequency range. The application of a continuous spectrum in the analysis of experimental data allows one to use the conception of the truncation of a spectrum in transition to non-linear viscoelastic behavior of polymeric materials.

Nomenclature

$G(\tau)$	– relaxation spectrum
G_0	– instantaneous modules
G'	– storage modules
G''	– loss modules
K_0	– parameter of a continuous spectrum in Eq.3
K_n	– weigh of n -th relaxation time in a spectrum, Eq.1
N^-	– relaxing (after cessation of steady shear flow) first difference of normal stresses
N	– total number of lines in a discrete spectrum
n	– current number of a line in a discrete spectrum
S_N	– area under the normal stress relaxation curve
S_τ	– area under the shear stress relaxation curve
t	– time
X	– dimensionless parameter defined by Eq.9
α	– parameter (slope) of a continuous relaxation spectrum
β	– parameter in the equation for a discrete spectrum
$\dot{\gamma}$	– shear rate
Δ	– step between neighboring lines in a discrete spectrum
δ	– delta-function
η_0	– initial (Newtonian) viscosity
τ	– relaxation time
τ_{max}	– maximal relaxation time
ζ_0	– initial coefficient of first difference of normal stresses
ω	– frequency

References

- Baumgärtel M. and Winter H.H. (1989): *Determination of the discrete relaxation and retardation time spectra from dynamic mechanical data.* – Rheol. Acta, vol.28, No.6, pp.511-519.
- Baumgärtel M. and Winter H.H. (1992): *Interrelation between continuous and discrete relaxation time spectra.* – J. Non-Newton. Fluid Mech., vol.44, No.1-2, pp.15-36.
- Elser J.C., Honerkamp J. and Weese J. (1992): *Using regularization methods for determination of relaxation and retardation spectra of polymeric liquids.* – Rheol. Acta, vol.31, No.2, pp.161-174.
- Emri I. and Tschoegl N.W. (1993): *Generating line spectra from experimental responses, Part I. Relaxation modulus and creep compliance.* – Rheol. Acta, vol.32, No.3, pp.311-312.
- Ferry J.D. (1980): *Viscoelastic Properties of Polymers.* – New York, Wiley.
- Gross B. (1953): *Mathematical Structure of the Theories of Viscoelasticity.* – Paris, Hermann.

- Honerkamp J. (1989): *Ill posed problems in rheology*. – Rheol. Acta, vol.28, No.5, pp.363-371
- Honerkamp J., Weese J. (1989): *Determination of the relaxation spectrum by a regularization method*. – Macromolecules, vol. 22, No.11, pp.4372-4377.
- Jackson J, DeRosa M. and Winter H.H. (1994): *Molecular weight dependence of relaxation time spectra for the entanglement and flow behavior of monodisperse linear flexible polymers*. – Macromolecules, vol.27, No.9, pp.2426-2471.
- Malkin A.Ya. (1968): *Normal stresses and relaxation spectra of polymeric systems* (in French). – Rheol. Acta, vol.7, No.4, pp.335-340.
- Malkin A.Ya. (1990): *Some inverse problems in rheology leading to integral equations*. – Rheol. Acta, vol.29, No.6, pp.512-518.
- Malkin A.Ya. and Kuznetsov V.V. (2000): *Linearization as a method for determining parameters of relaxation spectra*. – Rheol. Acta, vol.39, No.3, pp.379-383.
- Malkin A.Ya. and Masalova I. (2001): *From dynamic modulus via different relaxation spectra to relaxation and creep functions*. – Rheol. Acta, vol.40, No.3, pp.261-271.
- Malkin A.Ya. (2002): *The sense of a relaxation spectrum and methods for its calculation*. – Vysokomol. Soedin. (Polymers – in Russian), vol.44, No.9, pp.1698-2005.
- Sohn S. and Rajagopalan R. (2004): *Miscorheology of model quasi-hard-sphere dispersions*. – J. Rheol., vol.48, No.1, pp.117-142.
- Tschoegl N.W. (1989): *The Phenomenological Theory of Linear Viscoelasticity. An Introduction*. – Berlin: Springer.
- Tschoegl N.W. and Emri I (1993): *Generating line spectra from experimental responses, Part II. Storage and loss functions*. – Rheol. Acta, vol.32, No.3, pp.322-327.
- Vinogradov G.V. and Malkin A.Ya. (1989): *Rheology of Polymers*. – Berlin: Springer.
- Winter H.H. (1997): *Analysis of dynamic mechanical data: inversion into a relaxation time spectrum and consistency check*. – J. Non-Newton, Fluid Mech., vol.68, No.2/3, pp.225-239.

Received: April 30, 2005