

# Exact Relationships in Phenomenological Analysis of Rheodynamic Relaxation / Retardation Processes in Linear Viscoelasticity of Polymer Systems

## II.2. Secondary Characteristic Quantities in the Case of Stress - Controlled Processes

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*The secondary rheodynamic quantities in case of stress ( $\sigma$ )-controlled retardation processes, including the storage, loss and absolute moduli, as well as the corresponding loss factor, are considered from the viewpoint of frequency dependence, exact relationships providing the  $\sigma$  - characteristic frequencies corresponding to maximum and inflection points being given for the (1,1) - standard linear viscoelastic model. The results are illustrated in natural, semi-logarithmic, logarithmic and double-logarithmic coordinate representations.*

*Keywords: Exact relationships, rheodynamic retardation, linear viscoelasticity, polymer systems*

Appropriate assessment of rheological behaviour of polymer materials in the framework of linear viscoelasticity strongly recommends the use of dynamic characterization [1-9]. Accordingly, the two distinct lines involving the strain( $\varepsilon$ )- and stress( $\sigma$ )-controlled processes, respectively, providing in a straight manner primary and secondary rheodynamic quantities, are to be considered together with the modulus-compliance interrelationships. Finally, the comprehensive (primary-secondary) description being accomplished in the  $\varepsilon$ -controlled case [1,3], that of  $\sigma$ -controlled one [2] is considered for the secondary counterpart for different typical coordinate representations used in the circumstances of standard linear viscoelastic model.

### General definitions

In the general case of *solid linear viscoelastic behaviour*, the rheological equation for the (m,n)- *rheological state* can be expressed in terms of P, Q differential operators as

$$Q_{(n)}\varepsilon = P_{(m)}\sigma \quad (\text{II.1})$$

where

$$Q_{(n)} = q_0 + q_1 D_t + q_2 D_t^{(2)} + \dots + q_n D_t^{(n)} \quad (\text{II.2.1})$$

$$P_{(m)} = p_0 + p_1 D_t + p_2 D_t^{(2)} + \dots + p_m D_t^{(m)} \quad (\text{II.2.2})$$

and  $\varepsilon$ ,  $\sigma$  denote the *natural rheological variables*,  $q_0, q_1, q_2, \dots, q_n$ ;  $p_0, p_1, p_2, \dots, p_m$  are the *nominal rheological parameters*, while  $D_t^{(r)} = d^r/dt^r$  represents the r-th order time derivative operator, and  $m \leq n$ .

As previously established [2], in the case of a *sinusoidal stress-controlled process* of given amplitude,  $\sigma_0$ , and circular frequency,  $\omega$ ,

$$\tilde{\sigma} = \sigma_0 \exp(i\omega t) \quad (\text{II.3})$$

the corresponding *steady-state strain* is of the form

$$\tilde{\varepsilon} = \varepsilon_0(\omega) \exp\{i[\omega t - \delta_{(m,n)}(\omega)]\} \quad (\text{II.4})$$

and, by definition

$$\tilde{\varepsilon} / \tilde{\sigma} = [\varepsilon_0(\omega) / \sigma_0(\omega)] \{ \cos[\delta_{(m,n)}(\omega)] - i \sin[\delta_{(m,n)}(\omega)] \} \quad (\text{II.5})$$

is the *complex compliance*

$$J_{(m,n)}^*(\omega) = J'_{(m,n)}(\omega) - iJ''_{(m,n)}(\omega) \quad (\text{II.6})$$

whereas in the case of a *sinusoidal strain-controlled process* of given amplitude,  $\varepsilon_0$ , and circular frequency,  $\omega$ , [1],

$$\tilde{\varepsilon} = \varepsilon_0 \exp(i\omega t) \quad (\text{II.7})$$

the corresponding *steady-state stress* is of the form

$$\tilde{\sigma} = [\sigma_0(\omega)]_{(m,n)} \exp\{i[\omega t + \delta_{(m,n)}(\omega)]\} \quad (\text{II.8})$$

and, by definition

$$\tilde{\sigma} / \tilde{\varepsilon} = [\sigma_0(\omega) / \varepsilon_0(\omega)]_{(m,n)} \{ \cos[\delta_{(m,n)}(\omega)] + i \sin[\delta_{(m,n)}(\omega)] \} \quad (\text{II.9})$$

denotes the *complex modulus*

$$M_{(m,n)}^*(\omega) = M'_{(m,n)}(\omega) + iM''_{(m,n)}(\omega) \quad (\text{II.10})$$

In the case of  $\sigma$ -controlled dynamic process when the complex compliance,  $J_{(m,n)}^*$ , results in a direct manner, along with that of the  $\varepsilon$ -controlled one, when the corresponding complex modulus,  $M_{(m,n)}^*$ , is provided, the key relationship occurs

$$J_{(m,n)}^*(\omega) M_{(m,n)}^*(\omega) = 1 \quad (\text{II.11})$$

In case of  $\sigma$ -controlled processes, the complex compliance,  $J_{(m,n)}^*(\omega)$  is given by *direct primary rheodynamic quantities* - the (m,n)-storage compliance,

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$J_{(m,n)}$ ,  $(\omega)$ , and the (m,n)-loss compliance,  $J_{(m,n)}^*$ ,  $(\omega)$ , or by using the *derived primary rheodynamic quantities* - the (m,n)-absolute compliance,  $|J_{(m,n)}^*|$ ,  $(\omega)$ , and the (m,n)-loss factor,  $\beta_{J_{(m,n)}^*}$ ,  $(\omega)$  - whereas the corresponding complex modulus,  $M_{J_{(m,n)}^*}^*$ ,  $(\omega)$ , results in terms of *secondary rheodynamic quantities* - the storage modulus  $M_{J_{(m,n)}^*}$ ,  $(\omega)$ , and the loss modulus,  $M_{J_{(m,n)}^*}^*$ ,  $(\omega)$ , defined as

$$M_{J_{(m,n)}^*}^*(\omega) = M_{J_{(m,n)}^*}'(\omega) + iM_{J_{(m,n)}^*}''(\omega) \quad (II.12)$$

which can be calculated by using the relationships

$$M_{J_{(m,n)}^*}'(\omega) = J_{M_{(m,n)}^*}'(\omega) / |J_{M_{(m,n)}^*}^*|^2 \quad (II.13)$$

$$M_{J_{(m,n)}^*}''(\omega) = J_{M_{(m,n)}^*}''(\omega) / |J_{M_{(m,n)}^*}^*|^2 \quad (II.14)$$

as well as those for the absolute modulus,  $|M_{J_{(m,n)}^*}^*|$ ,  $(\omega)$ , given as

$$|M_{J_{(m,n)}^*}^*| = [M_{J_{(m,n)}^*}'^2(\omega) + M_{J_{(m,n)}^*}''^2(\omega)]^{1/2} \quad (II.15)$$

and the corresponding loss factor,  $\beta_{M_{J_{(m,n)}^*}^*}(\omega)$  assigned by

$$\begin{aligned} \beta_{M_{J_{(m,n)}^*}^*}(\omega) &= \tan \delta_{M_{J_{(m,n)}^*}^*}(\omega) = M_{J_{(m,n)}^*}''(\omega) / M_{J_{(m,n)}^*}'(\omega) = \\ &= J_{M_{(m,n)}^*}''(\omega) / J_{M_{(m,n)}^*}'(\omega) = \tan \delta_{J_{M_{(m,n)}^*}^*}(\omega) = \beta_{J_{M_{(m,n)}^*}^*}(\omega) \end{aligned} \quad (II.16)$$

### $\sigma$ - (1, 1) rheological state frequency effects

For the model of *standard linear viscoelastic solid* which states the situation when  $m=n=1$ , i. e., the mono-relaxant/mono-retardant case, the arising rheological equation of the (1,1)-*rheological state* is, [2],

$$p_0 \sigma + q_1 D_t \sigma = p_0 \sigma + p_1 D_t \sigma \quad (II.17)$$

The use of definition relationships, (II.10, II.11), /2/, and (II.13-II.16) provides the set of *secondary  $\sigma$ -controlled rheodynamic quantities* -  $M_{J_{(1,1)}^*}'$ ,  $M_{J_{(1,1)}^*}''$ ,  $|M_{J_{(1,1)}^*}^*|$  and  $\beta_{M_{J_{(1,1)}^*}^*}(\omega)$  on the basis of *primary* ones.

In terms of *nominal* rheological parameters results

$$M_{J_{(1,1)}^*}'(\omega) = (p_0 q_0 + p_1 q_1 \omega^2) / (p_0^2 + p_1^2 \omega^2) \quad (II.18.1)$$

$$M_{J_{(1,1)}^*}''(\omega) = (p_0 q_1 - p_1 q_0) \omega / (p_0^2 + p_1^2 \omega^2) \quad (II.18.1)$$

$$|M_{J_{(1,1)}^*}^*| = [(q_0^2 + q_1^2 \omega^2) / (p_0^2 + p_1^2 \omega^2)]^{1/2} \quad (II.18.1)$$

$$\beta_{M_{J_{(1,1)}^*}^*}(\omega) = (p_0 q_1 - p_1 q_0) \omega / (p_0 q_0 + p_1 q_1 \omega^2) \quad (II.18.1)$$

and if the *characteristic* rheological parameters

$$C_0 = p_0 / q_0, C_1 = p_1 / q_0, D_1 = q_1 / q_0 \quad (II.19)$$

are used, one gets

$$M_{J_{(1,1)}^*}'(\omega) = (C_0 + C_1 D_1 \omega^2) / (C_0^2 + C_1^2 \omega^2) \quad (II.20.1)$$

$$M_{J_{(1,1)}^*}''(\omega) = (C_0 D_1 - C_1) \omega / (C_0^2 + C_1^2 \omega^2) \quad (II.20.2)$$

$$|M_{J_{(1,1)}^*}^*| = [(1 + D_1^2 \omega^2) / (C_0^2 + C_1^2 \omega^2)]^{1/2} \quad (II.20.3)$$

$$\beta_{M_{J_{(1,1)}^*}^*}(\omega) = (C_0 D_1 - C_1) \omega / (C_0 + C_1 D_1 \omega^2) \quad (II.20.4)$$

Given the *limit* values for storage modulus are

$$\lim_{\omega \rightarrow 0} M_{J_{(1,1)}^*}'(\omega) = M_0' = 1 / C_0 = 1 / J_0' \quad (II.22.1)$$

$$\lim_{\omega \rightarrow \infty} M_{J_{(1,1)}^*}'(\omega) = M_\infty' = D_1 / C_1 = 1 / J_\infty' \quad (II.22.2)$$

and  $D_1 (= \tau_\sigma)$  is defined as a time dimension quantity, traditionally termed as the "*retardation time*", even if it is visible that the  $D_1 = 1/\omega_\tau$  definition, where  $\omega_\tau$  is a *characteristic frequency* seems to be more suitable, functional relationships arise.

Accordingly,

$$M_{J_{(1,1)}^*}'(\omega) = (J_0' + J_\infty' \tau_\sigma^2 \omega^2) / (J_0'^2 + J_\infty'^2 \tau_\sigma^2 \omega^2) \quad (II.22.1)$$

$$M_{J_{(1,1)}^*}''(\omega) = (J_0' - J_\infty') \tau_\sigma \omega / (J_0'^2 + J_\infty'^2 \tau_\sigma^2 \omega^2) \quad (II.22.2)$$

$$|M_{J_{(1,1)}^*}^*| = [(1 + \tau_\sigma^2 \omega^2) / (J_0'^2 + J_\infty'^2 \tau_\sigma^2 \omega^2)]^{1/2} \quad (II.22.3)$$

$$\beta_{M_{J_{(1,1)}^*}^*}(\omega) = (J_0' - J_\infty') \tau_\sigma \omega / (J_0' + J_\infty' \tau_\sigma^2 \omega^2) \quad (II.22.4)$$

Furthermore, given the basic frequency significance of  $1 / \tau_\sigma$ ,

$$M_{J_{(1,1)}^*}'(\omega) = (J_0' + J_\infty' \omega^2 / \omega_\sigma^2) / (J_0'^2 + J_\infty'^2 \omega^2 / \omega_\sigma^2) \quad (II.23.1)$$

$$M_{J_{(1,1)}^*}''(\omega) = [(J_0' - J_\infty') \omega / \omega_\sigma] / (J_0'^2 + J_\infty'^2 \omega^2 / \omega_\sigma^2) \quad (II.23.2)$$

$$|M_{J_{(1,1)}^*}^*| = [(1 + \omega^2 / \omega_\sigma^2) (J_0'^2 + J_\infty'^2 \omega^2 / \omega_\sigma^2)]^{1/2} \quad (II.23.3)$$

$$\beta_{M_{J_{(1,1)}^*}^*}(\omega) = [(J_0' - J_\infty') \omega / \omega_\sigma] / (J_0' + J_\infty' \omega^2 / \omega_\sigma^2) \quad (II.23.4)$$

$\omega_\sigma$  being the frequency at which the loss compliance presents a *maximum value*, and can be defined as the *natural frequency* of the  $\sigma$  *controlled dynamic retardation process*. Finally,

$$M_{J_{(1,1)}^*}'(\omega_\sigma) = (J_0' + J_\infty' \omega_\sigma^2) / (J_0'^2 + J_\infty'^2 \omega_\sigma^2) \quad (II.24.1)$$

$$M_{J_{(1,1)}^*}''(\omega_\sigma) = [(J_0' - J_\infty') \omega_\sigma] / (J_0'^2 + J_\infty'^2 \omega_\sigma^2) \quad (II.24.2)$$

$$|M_{J_{(1,1)}^*}^*|(\omega_\sigma) = [(1 + \omega_\sigma^2) (J_0'^2 + J_\infty'^2 \omega_\sigma^2)]^{1/2} \quad (II.24.3)$$

$$\beta_{M_{J_{(1,1)}^*}^*}(\omega_\sigma) = [(J_0' - J_\infty') \omega_\sigma] / (J_0' + J_\infty' \omega_\sigma^2) \quad (II.24.4)$$

where  $\bar{\omega} = \omega / \omega_\sigma$  represents the corresponding *relative (normalized) frequency*.

### $\sigma$ - (1, 1) characteristic frequencies

In order to identify the main consequences of the obtained set of secondary rheo-dynamic quantities in case of  $\sigma$ -*controlled* processes, the corresponding first-,  $D_\omega$ , and second-order,  $D_\omega^{(2)}$ , frequency derivative are calculated, the solution of resulting equations providing the *necessary conditions* of maximum and inflection, respectively.

For the storage modulus, it follows

$$D_\omega M_{J_{(1,1)}^*}'(\omega) = 2C_0 C_1 (C_0 D_1 - C_1) \omega / (C_0^2 + C_1^2 \omega^2)^2 \quad (II.25.1)$$

$$D_\omega^{(2)} M_{J_{(1,1)}^*}'(\omega) = 2C_0 C_1 (C_0 D_1 - C_1) (C_0^2 - 3C_1^2 \omega^2) / (C_0^2 + C_1^2 \omega^2)^3 \quad (II.25.2)$$

the inflection frequency yielding as

$$\begin{aligned} \omega_{(M_{J_{(1,1)}^*}')} &= \text{sol}[D_\omega^{(2)} M_{J_{(1,1)}^*}'(\omega) = 0] = (\sqrt{3}/3)(C_0/C_1)_1 = \\ &= (\sqrt{3}/3)(J_0'/J_\infty')(1/\tau_\sigma) = (\sqrt{3}/3)(J_0'/J_\infty')\omega_\sigma \end{aligned} \quad (II.26.1)$$

In case of the loss modulus one obtains

$$D_{\omega} M_{J(1,1)}^* (\omega) = (C_0 D_1 - C_1)(C_0^2 - C_1^2 \omega^2) / (C_0^2 + C_1^2 \omega^2)^2 \quad (\text{II.27.1})$$

$$D_{\omega}^{(2)} M_{J(1,1)}^* (\omega) = 2C_1^2 (C_0 D_1 - C_1)(-3C_0^2 + C_1^2 \omega^2) \omega / (C_0^2 + C_1^2 \omega^2)^3 \quad (\text{II.27.2})$$

the corresponding maximum frequency being

$$\omega_{m(M_{J(1,1)}^*)} = \text{sol}[D_{\omega} M_{J(1,1)}^* (\omega) = 0] = C_0 / C_1 = (J'_0 / J'_\infty)(1 / \tau_{\sigma}) = (J'_0 / J'_\infty) \omega_{\sigma} \quad (\text{II.28.1})$$

whereas the inflection one is

$$\omega_{i(M_{J(1,1)}^*)} = \text{sol}[D_{\omega}^{(2)} M_{J(1,1)}^* (\omega) = 0] = \sqrt{3}(C_0 / C_1) = \sqrt{3}(J'_0 / J'_\infty)(1 / \tau_{\sigma}) = \sqrt{3}(J'_0 / J'_\infty) \omega_{\sigma} \quad (\text{II.29.1})$$

For the absolute modulus one gets

$$D_{\omega} |M_{J(1,1)}^* (\omega)| = (C_0^2 D_1^2 - C_1^2) \omega / [(C_0^2 + C_1^2 \omega^2)^{3/2} (1 + D_1^2 \omega^2)^{1/2}] \quad (\text{II.30.1})$$

$$D_{\omega}^{(2)} |M_{J(1,1)}^* (\omega)| = (C_0^2 D_1^2 - C_1^2)(C_0^2 - 2C_1^2 \omega^2 - 3C_1^2 D_1^2 \omega^4) / \{[(C_0^2 + C_1^2 \omega^2)^{5/2} (1 + D_1^2 \omega^2)^{3/2}]\} \quad (\text{II.30.2})$$

resulting for inflection

$$\omega_{i(M_J)} = \{\text{sol}^*[D_{\omega}^{(2)} M_J = 0] \rightarrow \text{sol}^*[3C_1^2 D_1^2 \omega^4 + 2C_1^2 \omega^2 - C_0^2 = 0]\} = (1/3C_1 D_1) \sqrt{3C_1 (\sqrt{3C_0^2 D_1^2 + C_1^2} - C_1)} = (\sqrt{3}/3)(1/D_1) \sqrt{\sqrt{1+3C_0^2/(C_1^2 D_1^2)} - 1} = (\sqrt{3}/3) \omega_{\sigma} \sqrt{\sqrt{1+3J_0'^2/J_\infty'^2} - 1} \quad (\text{II.31.1})$$

In the case of the corresponding loss factor

$$D_{\omega} \beta_{M_{J(1,1)}} (\omega) = (C_0 D_1 - C_1)(C_0 - C_1 D_1 \omega^2) / (C_0 + C_1 D_1 \omega^2)^2 \quad (\text{II.32.1})$$

$$D_{\omega}^{(2)} \beta_{M_{J(1,1)}} (\omega) = 2C_1 D_1 (C_0 D_1 - C_1)(-3C_0 + C_1 D_1 \omega^2) \omega / (C_0 + C_1 D_1 \omega^2)^3 \quad (\text{II.32.2})$$

the maximum condition gives

$$\omega_{m(\beta_{M_{J(1,1)}})} = \text{sol}[D_{\omega} \beta_{M_{J(1,1)}} (\omega) = 0] = \sqrt{C_0 / C_1 D_1} = \sqrt{J'_0 / J'_\infty} (1 / \tau_{\sigma}) = \sqrt{J'_0 / J'_\infty} \omega_{\sigma} \quad (\text{II.33.1})$$

while for the inflection one results

$$\omega_{i(\beta_{M_{J(1,1)}})} = \text{sol}[D_{\omega}^{(2)} \beta_{M_{J(1,1)}} (\omega) = 0] = \sqrt{C_0 / C_1 D_1} = \sqrt{J'_0 / J'_\infty} (1 / \tau_{\sigma}) = \sqrt{J'_0 / J'_\infty} \omega_{\sigma} \quad (\text{II.33.2})$$

As result of the explicit sequence of values

$$\sqrt{J'_0 / J'_\infty} < \sqrt{3J'_0 / J'_\infty} < (\sqrt{3}/3)(J'_0 / J'_\infty) < J'_0 / J'_\infty < \sqrt{3}(J'_0 / J'_\infty) \quad (\text{II.34.1})$$

and in virtue of the fact that for polymeric materials  $J'_0 > 10J'_\infty$ , the resulting physical consequence

$$\omega_{i(M_J)} < \omega_{m(\beta_{M_J})} < \omega_{i(\beta_{M_J})} < \omega_{i(M_J')} < \omega_{m(M_J')} < \omega_{i(M_J')} \quad (\text{II.34.2})$$

expresses the existence, in the case of  $\sigma$ -controlled processes, for different secondary rheodynamic quantities of a full set of  $\sigma$ -characteristic frequencies. The relationships for the frequencies corresponding to the complete set of primary and secondary viscoelastic quantities are given in table 1.

**Table 1**  
CHARACTERISTIC FREQUENCIES CORRESPONDING TO PRIMARY AND SECONDARY RHEODYNAMIC QUANTITIES FOR  $\sigma$ -CONTROLLED PROCESSES

Viscoelastic Quantity	Frequency	Value
$J'$	$\omega_{(J')}$	$(\sqrt{3}/3)\omega_{\sigma}$
$J''$	$\omega_{m(J'')}$	$\omega_{\sigma}$
$J''$	$\omega_{i(J'')}$	$\sqrt{3}\omega_{\sigma}$
$J$	$\omega_{(J)}$	$(\sqrt{3}/3)(J'_0 / J'_\infty)\omega_{\sigma} \sqrt{\sqrt{1+3J_0'^2/J_\infty'^2} - 1}$
$BJ$	$\omega_{m(\beta_J)}$	$\sqrt{J'_0 / J'_\infty} \omega_{\sigma}$
$BJ$	$\omega_{i(\beta_J)}$	$\sqrt{3} \sqrt{J'_0 / J'_\infty} \omega_{\sigma}$
$M'_J$	$\omega_{(M'_J)}$	$(\sqrt{3}/3)(J'_0 / J'_\infty)\omega_{\sigma}$
$M''_J$	$\omega_{m(M''_J)}$	$(J'_0 / J'_\infty)\omega_{\sigma}$
$M''_J$	$\omega_{i(M''_J)}$	$\sqrt{3}(J'_0 / J'_\infty)\omega_{\sigma}$
$M_J$	$\omega_{(M_J)}$	$(\sqrt{3}/3)\omega_{\sigma} \sqrt{\sqrt{1+3J_0'^2/J_\infty'^2} - 1}$
$B_{M_J}$	$\omega_{m(\beta_{M_J})}$	$\sqrt{J'_0 / J'_\infty} \omega_{\sigma}$
$B_{M_J}$	$\omega_{i(\beta_{M_J})}$	$\sqrt{3} \sqrt{J'_0 / J'_\infty} \omega_{\sigma}$

Taking into account the results obtained for  $\varepsilon$ - and  $\sigma$ -controlled primary rheodynamic quantities, [1, 2], the two basic relationships,

$$\omega_{\varepsilon} = (J'_0 / J'_\infty) \omega_{\sigma} \quad (\text{II.35})$$

$$\omega_{\sigma} \omega_{\varepsilon} = \omega_{\text{or}}^2 \quad (\text{II.36})$$

among many others, are pointed out, where  $\omega_{\varepsilon}$  represents the natural frequency of the  $\varepsilon$ -controlled rheodynamic process, to which corresponds the maximum of loss modulus, and  $\omega_{\sigma\varepsilon}$  is the  $\sigma\varepsilon$ -characteristic mixed frequency corresponding to the maximum value of loss factor, each quantity providing a distinct criterion for appropriate assessing of the material behaviour potential.

### Simulation of secondary (1, 1) - rheodynamic effects

In order to point out the peculiarities of frequency dependence in the case of different secondary  $\sigma$ -controlled rheodynamic processes, physically realistic values of  $J'_0$ ,  $J'_\infty$ ,  $\omega_{\sigma}$  are considered, e.g.,

$$J'_0 = [1 / \text{MPa}], J'_\infty = 10^{-3} [1 / \text{MPa}], \omega_{\sigma} = 1, 2, 5 [\text{rad} / \text{s}]$$

The obtained results are given in figure II.1 for the storage modulus (M1J), in figure II.2 - for the loss modulus (M2J), as well as in figure II.3 for the absolute modulus (MJ), and in figure II.4 - for the corresponding loss factor (BMJ), taking into account different standard coordinate representations - natural(a), semi-logarithmic(b), logarithmic(c) and double-logarithmic(d).

The calculated values of characteristic frequencies for given  $\sigma$ -controlled dynamic processes are given in table 2.

The dissimilar features of frequency dependence of different  $\sigma$ -controlled secondary rheodynamic quantities in case of (1, 1) - rheological behavior, draw attention, on the hand, for the storage modulus (fig. II.1), on the increase with increasing frequency, from the low value,  $M'_0$ , at zero

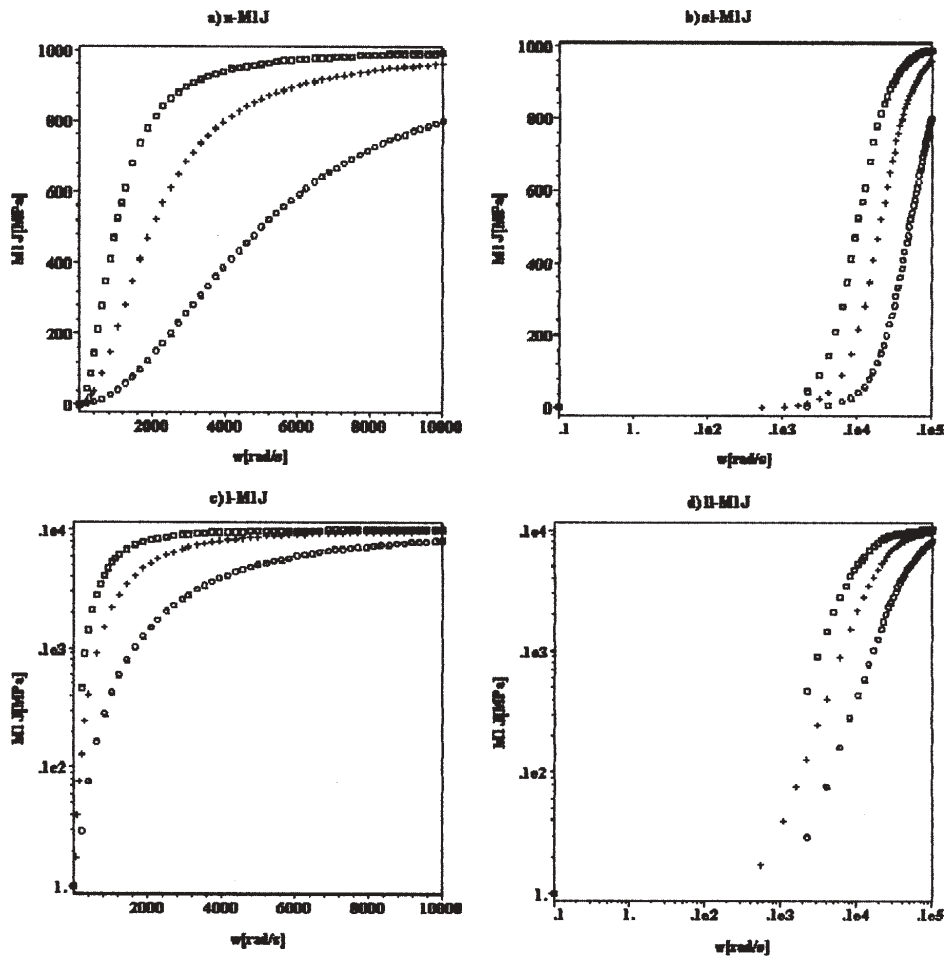


Fig. II.1 Storage modulus, M1J, versus frequency,  $\omega$ , for different dynamic *retardation* processes -  $\omega_{ret} = 1(\square)$ ,  $2(+)$ ,  $5(o)$  [rad/s] - in natural(a), semi-logarithmic(b), logarithmic(c) and double-logarithmic(d) coordinate representations

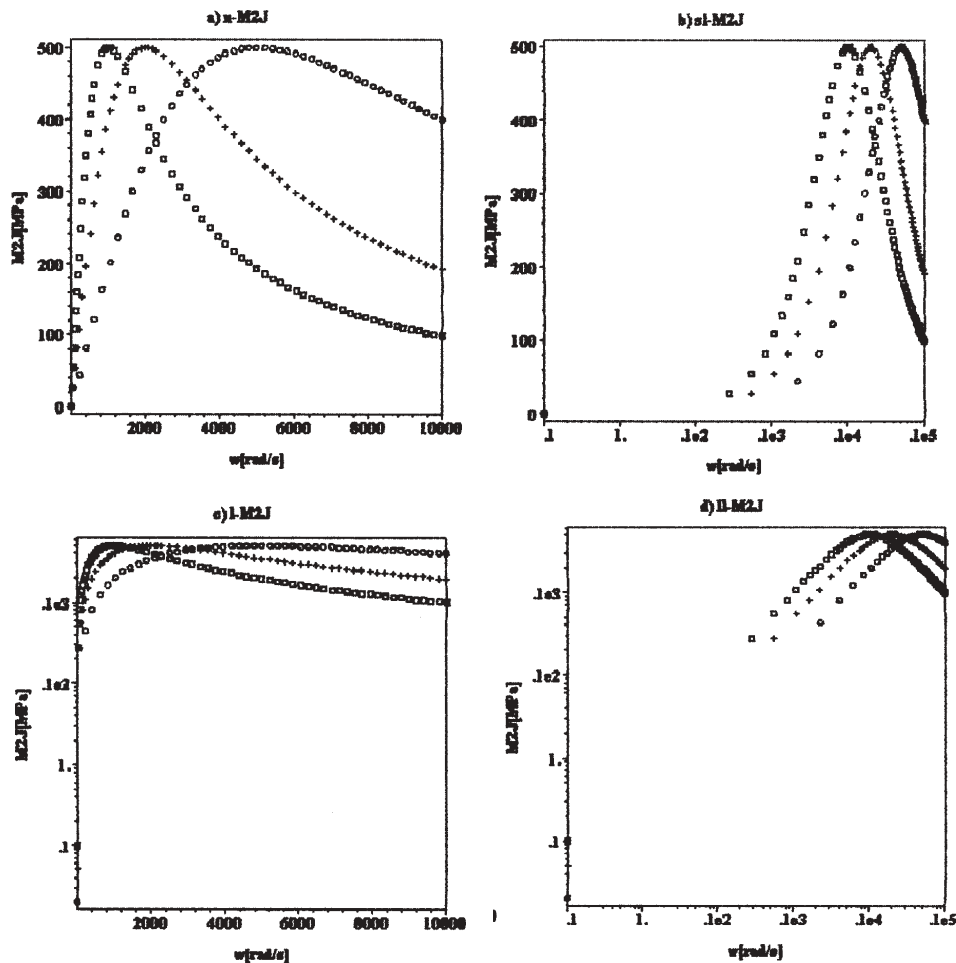


Fig. II.2 Loss modulus, M2J, versus frequency,  $\omega$ , for different dynamic *retardation* processes -  $\omega_{ret} = 1(\square)$ ,  $2(+)$ ,  $5(o)$  [rad/s] - in natural(a), semi-logarithmic(b), logarithmic(c) and double-logarithmic(d) coordinate representations

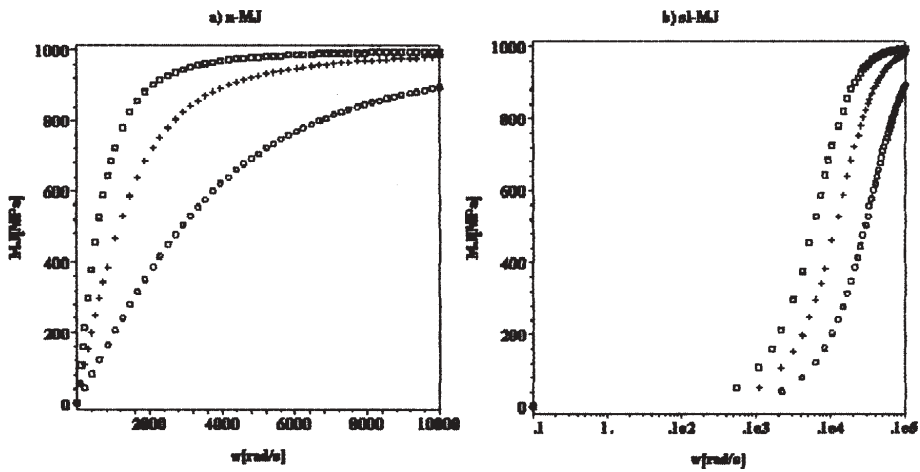


Fig. II.3 Absolute modulus, MJ, versus frequency,  $\omega$ , for different dynamic retardation processes -  $\omega_{ret} = 1(\square)$ ,  $2(+)$ ,  $5(o)$  [rad/s] - in natural(a), semi-logarithmic(b), logarithmic(c) and double-logarithmic(d) coordinate representations

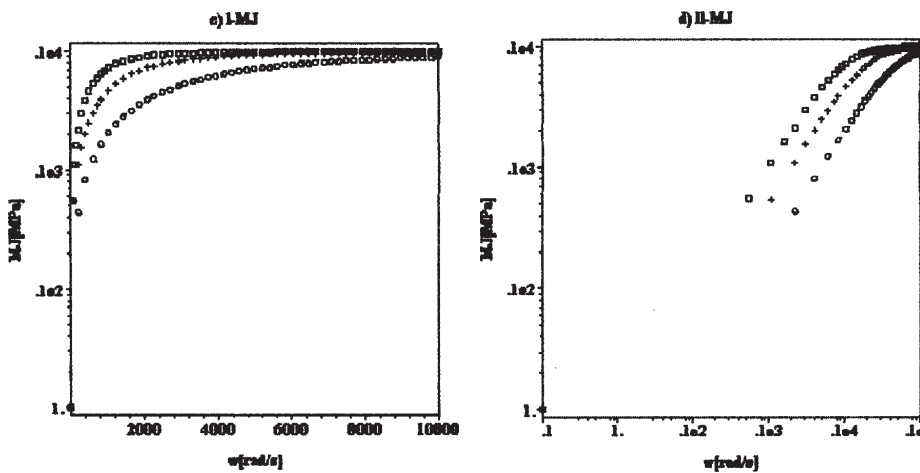
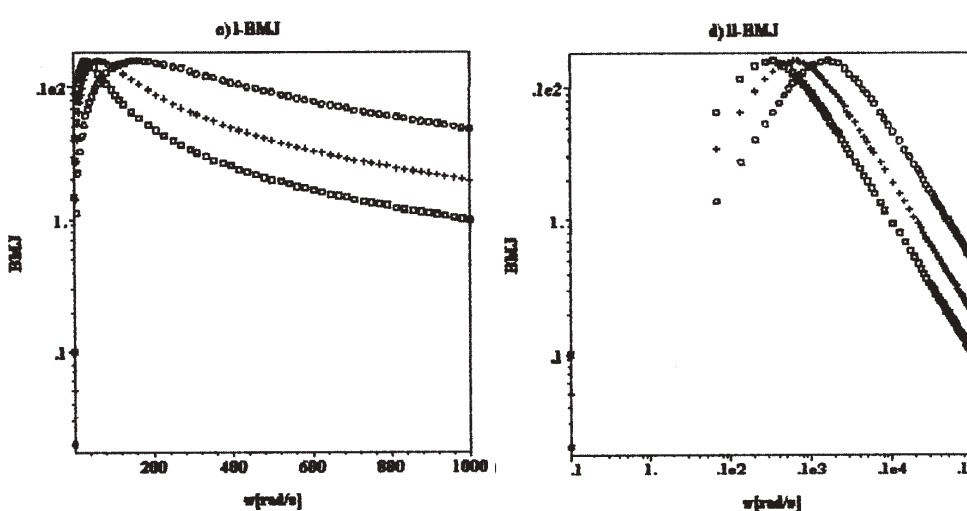
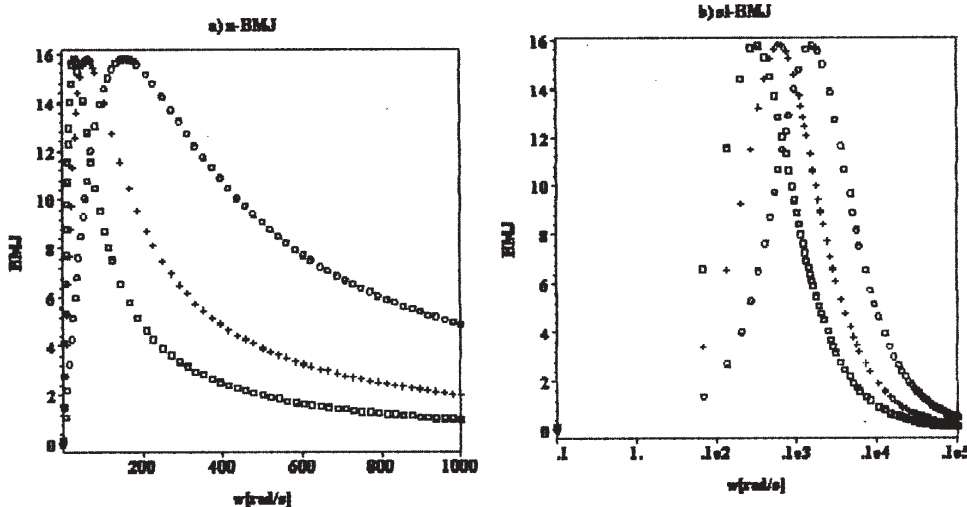


Fig. II.4 Loss factor, BMJ, versus frequency,  $\omega$ , for different dynamic retardation processes, -  $\omega_{et} = 1(\square)$ ,  $2(+)$ ,  $5(o)$  [rad/s] - in natural(a), semi-logarithmic(b), logarithmic(c) and double-logarithmic(d) coordinate representations



**Table 2**  
CALCULATED VALUES OF CHARACTERISTIC FREQUENCIES OF PRIMARY AND SECONDARY RHEODYNAMIC QUANTITIES IN CASE OF  $\sigma$ -CONTROLLED PROCESSES FOR GIVEN VALUES OF RETARDATION FREQUENCIES ( $W_{RET} = 1, 2, 5 \text{ RAD/S}$ )

Viscoelastic Quantity	Characteristic frequencies [rad/s]			
	J1	wi{J1}	0.57735	1.154701
J2	wm{J2}	1	2	5
	wi{J2}	1.732051	3.464102	8.660255
J	wi{J}	0.707107	1.4142	3.536
BJ	wm{BJ}	31.62277	63.246	158.114
	wi{BJ}	54.77226	109.545	273.861
M1J	wi{M1J}	577.35	1154.701	2888.751
M2J	wm{M2J}	1000	2000	5000
	wi{M2J}	1732.051	3464.102	8660.254
MJ	wi{MJ}	24.02118	48.0423	120.105
BMJ	wm{BMJ}	31.62277	63.246	158.114
	wi{BMJ}	54.77226	109.545	273.861

frequency, to the *high limit* value,  $M'_{\infty}$ , at “*infinite*” frequency; on the other hand, (fig. II.2), the loss modulus shows a *maximum, peak* value at intermediate frequency, corresponding to natural  $\varepsilon$  - frequency of dynamic relaxation process, while zero value corresponds both to *zero* and “*infinite*” frequency. For other *secondary* rheodynamic quantities distinct trends are evidenced - the absolute modulus, (fig. II.3), shows a frequency dependence similar to that of storage modulus, with inflection at lower frequency than in case of storage modulus, while the corresponding loss factor, (fig. II.4), shows a somewhat similitude with that of the loss modulus, even if the maximum and inflection frequencies are at lower values.

### Conclusions

In the case of *stress - controlled dynamic retardation processes* the set of  $\sigma$ -characteristic frequencies defined in terms of model rheological parameters is obtained, providing *complete information* as regards the spectrum of linear viscoelastic behaviour.

The *secondary* rheodynamic quantities - including in case of  $\sigma$ -*controlled* processes, on the hand, the storage and loss moduli, as well as, on the other hand, the absolute modulus and the corresponding loss factor, respectively - result on the basis of compliance-like ones, specific features being revealed by using the multiple criterium of characteristic maximum and/or inflection points.

Given the essential justification of usefulness of the set of characteristic frequencies in case of  $\sigma$  - *controlled dynamic retardation processes*, thoroughly attention is to be considered jointly for consistent characterization and appropriate evaluation of polymeric materials undergoing dynamic stress-controlled conditions of testing.

### References

1. PAVEN H., Materiale Plastice, **40**, nr. 4, 2003, p.171
2. PAVEN H., Mat. Plast., **41**, nr. 2, 2004, p.57
3. PAVEN H., Mat. Plast., **43**, nr. 4, 2006, p. 345
4. TOBOLSKY A. V., Properties and Structure of Polymers, Wiley, New York, 1960
5. LEITMAN M. J., FISCHER G. M. C., The Linear Theory of Viscoelasticity, in: FLUGGE S., ed., Encyclopedia of Physics, Vol. VIa/3, Springer, Berlin, 1973
6. GRUENWALD G., Plastics-How Structure Determines Properties, Hanser, Munich, 1992
7. MILLS N. J., Plastics-Microstructure and Engineering Applications, Arnold, London, 1993
8. ARIE R., Fundamentals of Polymer Engineering, Plenum Press, New York, 1997
9. SHAW M. T., MacKnight W. J., Introduction to Polymer Viscoelasticity, Wiley-Interscience, New York, 2005

Intrat în redacție: 19.01.2007