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ORIGINAL CONTRIBUTION

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Evaluation of molecular weight distribution from dynamic moduli

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Abstract A method to evaluate molecular weight distribution (MWD) from dynamic moduli is presented here. It relies on the least-square fitting of the dynamic data to a model whose parameters depend on the MWD. In particular, the *analytical solution* for the relaxation modulus previously obtained from the double reptation model, with the Tuminello step relaxation function and the Generalized Exponential Function (GEX) describing the MWD (Nobile and Cocchini 2000), has been used. A Finite Element Approximation (FEA) has been applied to calculate dynamic moduli from the relaxation modulus as a function of MWD. The sensitiveness of the GEX-double reptation dynamic moduli on the model parameters has also been investigated and the results show that large changes of the M_w/M_n ratio weakly affect the dynamic moduli, while small changes of the M_z/M_w ratio significantly deform the dynamic moduli curves. The use of rheological data to obtain MWD, by the model used in this paper, will, therefore, be able to give rather well defined M_z/M_w ratios, while more uncertainty will be presented in the M_w/M_n results. The so-called GEX-rheological model for the dynamic moduli was applied to fit the experimental data of different polymers in order to obtain the best-fit parameters of the MWD of these polymers, *without the need for the inversion* of the double reptation integral equation. The stability of the results has been confirmed through the evaluation of the 90% confidence intervals for the first molecular weight averages. Finally, concerning the M_w and M_z values, the predictions obtained from the dynamic moduli measurements differ by less than 10% from those obtained from GPC measurements while, as expected, more uncertainty is present in the M_n predictions.

Key words Dynamic moduli · Viscoelasticity · Polydispersity

Introduction

In the literature different mixing rules describe the rheological behavior of polydisperse polymers in terms of their molecular weight distribution (MWD) combining the relaxation features of the monodisperse components (Graessley and Struglinski 1986; Rubinstein and Colby 1988; Tsenoglou 1987, 1991; Des Cloiseaux 1988, 1990; Cassagnau et al. 1993). Among these, the concept of double reptation proposed by Tsenoglou (1987, 1991) and Des Cloiseaux (1988) has been used by Wasserman and Graesslay (1992, 1996) to calculate the dynamic moduli from known MWDs. More recently Nobile and Cocchini (2000) *analytically* computed the relaxation modulus, as well as the two material properties, the zero-shear rate viscosity and the steady state compliance, of polydisperse polymers on the basis of the double reptation model with the choice of the Tuminello step relaxation function (Tuminello 1986) and of the Generalized Exponential Function (GEX) (Gloor 1978, 1983) describing the MWD.

The inverse problem of obtaining the MWD both from the linear viscoelastic behavior (Tuminello 1986; Mead 1994; Anderssen et al. 1997; Anderssen and Mead 1998; Maier et al. 1998; Nobile et al. 1996a; Carrot and Guillet 1997) as well as from the flow curve of entangled polymer melts (Malkin and Teishev 1991; Shaw and Tuminello 1994; Liu et al. 1998; Nobile et al. 1996b) has been amply discussed in the literature. In all cases it has been emphasized that the solution of the inverse problem can be ill-posed; i.e., the solution might be extremely sensitive to small changes in the input. To overcome the possible ill-posed situation, in a previous study (Nobile et al. 1996b) some prior knowledge of the nature of the solution has been incorporated into the functional equation correlating the MWD to the viscosity. Indeed, among the different constraints that could be chosen, it was decided to assign an analytical MWD function directly to the transform, regardless of the knowledge of the actual MWD. Of course, such a constraint had to be flexible so as to avoid the loss of information from rheological data. The generalized exponential function (GEX) has been chosen among the different functions that describe MWDs since it is capable of accurately reproducing the MWD of a wide class of unimodal polymers (Gloor 1978, 1983), including most of the largely used MWD functions; i.e., the most probable, the Tung-Weibull, and so forth. The inclusion of the GEX function directly into the Malkin and Teishev (1991) or Bersted model (Bersted 1975) enabled us to obtain the *analytical* solution of the so-called GEX rheological model for the *viscosity*, whose parameters are connected to the MWD. This was applied to fit the experimental flow curve data in order to obtain the best-fit parameters, without the need for the inversion of the viscosity integral equation.

First attempts were also made with dynamic data (Nobile et al. 1996a). Following that idea, in the present paper, the *analytical* solution of the double reptation GEX model (Nobile and Cocchini 2000) is used to obtain the MWDs of entangled polydisperse polymers from their *linear viscoelastic* behavior. Indeed, the *analytical* results for the relaxation modulus as a function of the MWD parameters are used here to fit the experimental dynamic moduli data and to obtain the best-fit parameters related to the MWD. In this regard it has been necessary to connect the relaxation modulus to the dynamic moduli via well known relationships (Ferry 1980). In particular, in order to evaluate the dynamic moduli in an efficient and accurate numeric way, a Finite Element Approximation (FEA) technique has been used, as described in detail in the following sections. The sensitiveness of the dynamic moduli on the parameters of the model has also been discussed. Such an issue is, in fact, particularly stressful to define the reliability of the MWD parameters that are obtained from the rheological measurements. Then, dynamic data of different polydisperse polymers have been fitted to the GEX-double reptation model to compute the first molecular weight averages of the GEX distribution. Analogous to the case of obtaining the MWD parameters from the flow curve (Nobile et al. 1996b), in this case the stability of the solution has also been investigated through the determination of the χ^2 surface in the space of the GEX parameters around the minimum. The confidence region at 90% of probability has been obtained for all the samples tested. Furthermore, the molecular weight averages of the distribution have been compared with the corresponding estimates reported from Gel Permeation Chromatography (GPC) measurements. In particular, the materials investigated are two commercial polymers, a copolyacetal Celcon M25 (Hoechst Celanese) (Nobile and Cocchini 1999) and a polypropylene P3 (Wasserman and Graessley 1996), as well as the two mixtures, M1 and M2, obtained by mixing nearly monodisperse polystyrenes (Wasserman and Graessley 1992).

Methodology

The GEX-double reptation model

The rheological behavior of polydisperse entangled polymers has been successfully described in terms of the double reptation model (Tsenoglou 1987, 1991; Des Cloizeaux 1988, 1990). It reads as

$$G(t) = G_N^0 \left[\int_0^\infty w(M) \sqrt{F(M,t)}\, dM \right]^2 \tag{1}$$

for a continuous distribution, where G(t) is the stress relaxation modulus, G_N^0 is the plateau modulus of the species, w(M) is the weight fraction distribution, and F(M,t) is the reduced relaxation function for monodisperse samples at time t of molecular weight M.

The Generalized Exponential Function (GEX) has been considered to describe the molecular weight distribution:

$$w_{GEX}(a, b, M_0, M) = \frac{b}{M_0 \Gamma\left(\frac{a+1}{b}\right)} \left(\frac{M}{M_0}\right)^a \exp\left[-\left(\frac{M}{M_0}\right)^b\right] \tag{2}$$

where Γ is the gamma function. The first molecular weight averages of the GEX distribution are

$$M_n = M_0 \Gamma\left(\frac{a+1}{b}\right) \Big/ \Gamma\left(\frac{a}{b}\right) \tag{3a}$$

$$M_w = M_0 \Gamma\left(\frac{a+2}{b}\right) \Big/ \Gamma\left(\frac{a+1}{b}\right) \tag{3b}$$

$$M_z = M_0 \Gamma\left(\frac{a+3}{b}\right) \Big/ \Gamma\left(\frac{a+2}{b}\right) \tag{3c}$$

and so on.

In a previous paper (Nobile and Cocchini 2000) we have shown that the predictions of linear viscoelastic properties mainly depend on the double reptation mixing rule assumption, in systems with a large number of components, while the choice of the relaxation function is not crucial. In particular, the Tuminello step function (Tuminello 1986) has been chosen for its mathematical simplicity; it reads as

$$F(M,t) = \begin{cases} 1 & t \le \tau_0(M) \\ 0 & t > \tau_0(M) \end{cases} \tag{4}$$

where $\tau_o(M)$ is the mean relaxation time of the component of weight M. Within the frame of the model, this time is connected to the zero shear-rate viscosity, η_0, as

$$\tau_0 = \frac{\eta_0}{G_N^0} \tag{5}$$

By using the well established power-law dependence of η_0 on the molecular weight, M, for the *monodisperse* polymer above a critical mass:

$$\eta_0 = k\,M^{\alpha} \tag{6}$$

with α and k depending on the species (but typically α is around 3.4), the M-dependence of $\tau_o(M)$ in the relaxation model is defined.

Using the GEX function (Eq. 2) in the double reptation model (Eq. 1) according to the Tuminello relaxation model (Eq. 4), and taking into account Eqs. (5) and (6), we have obtained the analytical solution for the relaxation modulus

$$G_{GEX}(a,b,\tau,G_N^0,t) = G_N^0\,\Gamma^2\left[\frac{a+1}{b}, \left(\frac{t}{\tau}\right)^{\frac{b}{\alpha}}\right] \Big/ \Gamma^2\left(\frac{a+1}{b}\right) \tag{7}$$

where

$$\tau = k\,M_0^{\alpha}/G_N^0\ , \tag{8}$$

with k defined in Eq. (6) and M_0 defined in Eq. (2). The model has six independent parameters, namely a, b, M_0, G_N^0, k, and α. Indeed, all the parameters are experimentally obtainable material parameters, that is to say the model does not include adjustable parameters.

FEA for dynamic moduli

The relaxation modulus G(t) is connected to the dynamic moduli via the well known relationships (Ferry 1980)

$$G'(\omega) = \omega \int_0^{\infty} G(t)\ \mathrm{Sin}(\omega t)\ dt \tag{9a}$$

$$G''(\omega) = \omega \int_0^{\infty} G(t)\ \mathrm{Cos}(\omega t)\ dt \tag{9b}$$

The above integrals cannot be performed analytically when the relaxation modulus is expressed including the GEX form (Eq. 7). Therefore, in order to get the dynamic moduli in an efficient and accurate numerical way a Finite Element Approximation (FEA) technique has been used. According to the FEA, the relaxation modulus has been approximated with a segmented linear function among the points of a time grid t_i, $i = 1, 2, \ldots N$

$$G(t) \approx \sum_{i=1}^{N-1} g(t_i, t_{i+1}, t)\left(G_i \frac{t - t_{i+1}}{t_i - t_{i+1}} + G_{i+1} \frac{t - t_i}{t_{i+1} - t_i}\right) \tag{10}$$

where the function g is defined as

$$g(t_i, t_{i+1}, t) = \begin{cases} 1 & t_i \le t < t_{i+1} \\ 0 & \text{otherwise} \end{cases} \tag{11}$$

and $G_i = G(t_i)$, see Fig. 1.

Using the piecewise linear function, the integrals in Eqs. (9a) and (9b) can be done analytically. After some rearrangements, it turns out

$$G'(\omega) = \sum_{i=1}^{N} H_i^{(1)}(\omega)\ G_i \tag{12a}$$

$$G''(\omega) = \sum_{i=1}^{N} H_i^{(2)}(\omega)\ G_i \tag{12b}$$

where the coefficients $H_i^{(j)}(\omega)$, for $j = 1, 2$, are given as

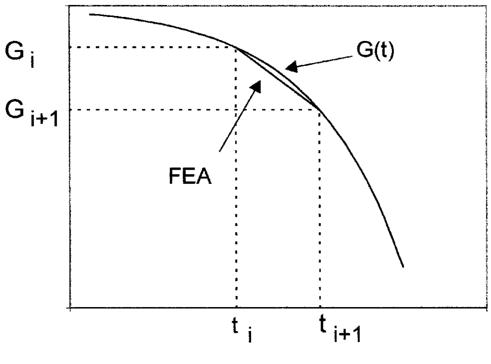

Fig. 1 FEA approximation for the relaxation modulus. The G(t) curve has been approximated with a segmented linear function among the points of a time grid t_i, $i = 1, 2, \ldots N$

$$H_i^{(j)}(\omega) = \begin{cases} h^{(j)}(t_2, t_1, \omega) & i = 1 \\ h^{(j)}(t_{i+1}, t_i, \omega) - h^{(j)}(t_{i-1}, t_i, \omega) & 1 < i < N \\ -h^{(j)}(t_{N-1}, t_N, \omega) & i = N \end{cases} \tag{13}$$

The functions $h^{(j)}$ are defined as

$$h^{(1)}(p, q, \omega) = \mathrm{Cos}(\omega q) + \frac{\mathrm{Sin}(\omega q) - \mathrm{Sin}(\omega p)}{(p - q)\omega} \tag{14a}$$

$$h^{(2)}(p, q, \omega) = -\mathrm{Sin}(\omega q) + \frac{\mathrm{Cos}(\omega q) - \mathrm{Cos}(\omega p)}{(p - q)\omega} \tag{14b}$$

The accuracy of the FEA technique has been tested on the single-exponential relaxation function, for which the exact dynamic moduli are known. Very good results have been obtained using log grids sufficiently wide and dense. As a rule of thumb, a grid of ten points per decade in a range exceeding two decades over and below the relaxation time has been chosen and it allows errors on the logarithm of the dynamic moduli less than 0.005. Some instabilities only arise in G'' at frequencies larger than the peak value. Indeed, this event does not influence our results that concern the terminal zone.

In the case of a general relaxation function, the "rule of thumb" applies to the relaxation spectrum, that is to say the time range should exceed the minimum and maximum time of the relaxation spectrum (which generates the relaxation modulus under study) of two decades.

The FEA technique is particularly suitable when there is the need to make repetitive calculations at given frequencies, as in the χ^2 minimization fitting procedure. Indeed, in that case it is necessary to compute only once the Hs at each frequency of interest (those corresponding to the experimental data set) and then to perform the summations in Eqs. 12a and 12b for each set of G_is. The FEA technique is also helpful in analyzing the dependence of dynamic moduli on the parameters of the model, as it will be investigated in the following section.

Sensitiveness of the GEX-double reptation dynamic moduli on the model parameters

Applying the FEA method to the relaxation modulus as obtained from the GEX-double reptation modulus (Eq. 7), it can be investigated how the dynamic moduli depend on the parameters of the model.

In order to fix the time grid, a rough estimate of the relaxation spectrum for a given parameter set $\{a, b, \tau, G_N^0\}$ is given by the Aury law (Ferry 1980):

$$H(\tau) \approx -\left.\frac{\partial G(t)}{\partial \ln t}\right|_{t=\tau} \tag{15}$$

and for the relaxation modulus as expressed by Eq. (7) it gives

$$H_{\mathrm{GEX}}(\tau) \approx \frac{2b}{\alpha} \frac{G_N^0}{\Gamma^2\left(\frac{a+1}{b}\right)} \Gamma\left[\frac{a+1}{b}, \left(\frac{t}{\tau}\right)^{\frac{b}{\alpha}}\right] \times \exp\left[-\left(\frac{t}{\tau}\right)^{\frac{b}{\alpha}}\right]\left(\frac{t}{\tau}\right)^{\frac{a+1}{\alpha}}$$

This formula has been applied to estimate a minimum and a maximum relaxation time (e.g., those times beyond which the spectrum falls three decades below its maximum). Then it has been used to generate the time range necessary for the FEA method; i.e., a time range exceeding the minimum and maximum time of the relaxation spectrum of two decades.

For the sake of discussion, it has been investigated how the model describes the MWD sensitivity. Scaling the data to τ and G_N^0, the results only depend on the a and b parameters. Furthermore, using Eq. (3), a and b can be associated to the M_w/M_n and M_z/M_w ratios. In Fig. 2 the results for $M_w/M_n = 2$ with $M_z/M_w = 1.5$ and 1.9 have been reported; while in Fig. 3 the results for $M_z/M_w = 2$ with $M_w/M_n = 2.1$ and 5 have been shown. It is evident how large changes of the M_w/M_n ratio weakly affect the dynamic moduli, while small changes of the M_z/M_w ratio significantly deform the dynamic moduli curves. Therefore, it can easily be inferred that the use of rheological data to obtain MWD, by the fitting to the model used in this paper, will be able to give rather well defined M_z/M_w ratios, while the M_w/M_n ratios will have large confidence intervals.

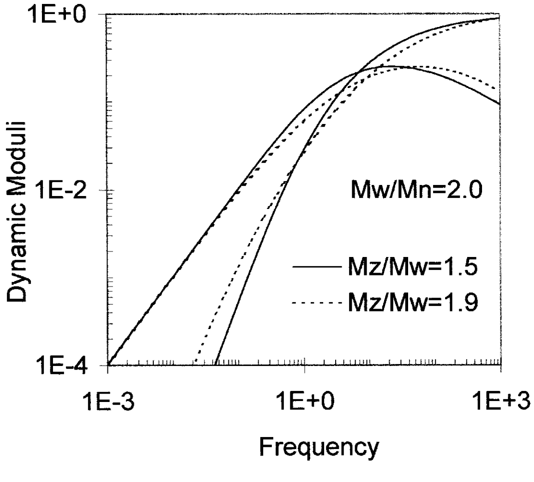

Fig. 2 Dynamic modulus curves as a function of frequency, as computed with FEA from the GEX-double reptation model. The parameters a and b have been chosen to get $M_w/M_n = 2$ with $M_z/M_w = 1.5$ and 1.9. The frequencies have been normalized to τ and the dynamic moduli to G_N^0

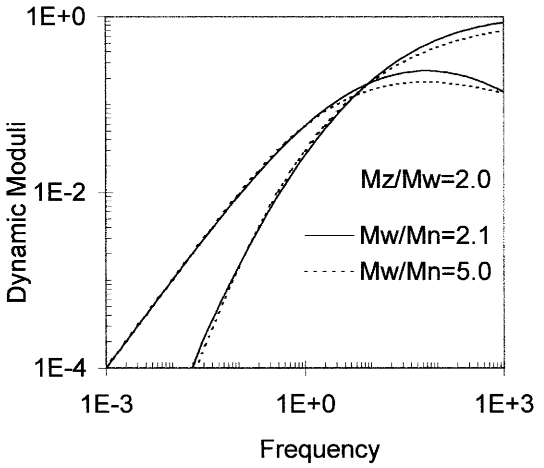

Fig. 3 Dynamic modulus curves as a function of frequency, as computed with FEA from the GEX-double reptation model. The parameters a and b have been chosen to get $M_z/M_w = 2$ with $M_w/M_n = 2.1$ and 5. The frequencies have been normalized to τ and the dynamic moduli to G_N^0

Fit procedure

In order to get MWD information from rheological measurements, the dynamic data $\{G_j'\}$ and $\{G_j''\}$ at a given frequency set $\{\omega_j\}$, j = 1, 2, ... Q, have been fitted to the GEX-double reptation model (Eq. 7), by a χ^2 minimization procedure. According to the FEA method (Eq. 12), the objective function is

$$\chi^2(a, b, \tau, G_N^0) = \sum_{j=1}^{Q} \left| G_j' - \sum_{i=1}^{N} M_i^{(1)}(\omega_j)\, G_{GEX}(a, b, \tau, G_N^0, t_i) \right|^2 + \sum_{j=1}^{Q} \left| G_j'' - \sum_{i=1}^{N} M_i^{(2)}(\omega_j)\, G_{GEX}(a, b, \tau, G_N^0, t_i) \right|^2$$

As discussed in a previous paper (Nobile et al. 1996b), the logarithms of the moduli have been considered to account for a constant relative error. In some cases the summations over the experimental frequencies, ω_j, can be limited to improve the results. In particular, the G′ data at small frequencies should be neglected since the GEX-double reptation model could be inaccurate (as discussed in Nobile and Cocchini 2000). On the other hand, at large frequencies the G″ FEA estimates from the GEX-double reptation model need too large time grids. Following these observations we have decided to stop the summation on G″ one decade beyond the G′-G″ crossover and to start the summation on G′ one decade before the crossover. Anyway, it has also been shown that the choice of the actual ranges of summation in Eq. (17) is not crucial, as it should be, in order to have reliable results.

To reduce the number of free parameters of the model some constraints can be considered. The analytical expression for the zero shear-rate viscosity in the GEX-double reptation model (Eq. 14 in Nobile and Cocchini 2000) is very useful to eliminate the τ parameter once η_0 has been assigned:

$$\tau = \frac{\eta_0}{G_N^0} \frac{\Gamma^2\left(\frac{a+1}{b}\right)\left(\frac{a+1}{b} + \frac{\alpha}{b}\right) 2^{\left(2\,\frac{a+1}{b} + \frac{\alpha}{b}\right)}}{2\,\Gamma\left(2\,\frac{a+1}{b} + \frac{\alpha}{b}\right) {}_2F_1\left(1, 2\,\frac{a+1}{b} + \frac{\alpha}{b};\, \frac{a+1}{b} + \frac{\alpha}{b} + 1;\, \frac{1}{2}\right)} \tag{18}$$

where ${}_2F_1$ is the hypergeometric function.

In principle, a similar expression for the steady-state compliance (Eq. 15 in Nobile and Cocchini 2000) could be used to estimate G_N^0. Unfortunately, this is of little help due to the large errors in the estimate of J_e^0 itself.

A way to estimate G_N^0 is through the sum rule:

$$G_N^0 = \frac{4}{\pi} \int_0^{\omega_{peak}} G'' \, d\ln\omega \tag{19}$$

where ω_{peak} is the frequency at which G″ attains a local maximum in the terminal zone (Ferry 1980). Indeed, the experimental curves often do not show that maximum in G″.

Alternative methods are proposed in the literature and applied to different homopolymers, such as the tan δ minimum criterion (Wu 1987) and the Wu relationship (Wu 1989). According to the former method, G_N^0 is the value obtained by G′ at the frequency where tan δ reaches its minimum in the rubbery plateau zone. The latter relationship correlates the ratio between the G′–G″ crossover and G_N^0 to the polydispersity. It read as

$$\log\left(\frac{G_N^0}{G_{cross}}\right) = 0.38 + \frac{2.63 \log p}{1 + 2.45 \log p} \tag{20}$$

where G_{cross} is the modulus at the crossover and $p = M_w/M_n$ should be less than about 3.

In the frame of the GEX model, a new method can be adopted: the G′–G″ crossover frequency can be used to obtain a somewhat more involved sum rule:

$$\gamma\, G_N^0 = \frac{4}{\pi} \int_0^{\omega_{cross}} G'' \, d\ln\omega \tag{21}$$

where $0 < \gamma < 1$. The γ value depends on the MWD shape and in the case of the GEX model it is a function of the a and b parameters only. It cannot be computed analytically, but it turns out that it is a weak function of the M_w/M_n and M_z/M_w ratios, as obtainable from Eq. (3). A working approximation, that will be used in the next section, is

$$\begin{aligned} \log(\gamma) = (&0.0103264 - 0.4781461\, L_1 \\ &+ 0.6028697\, L_1^2 - 1.0206309\, L_2 \\ &+ 1.4745246\, L_2^2 - 1.6073631\, L_1\, L_2) \end{aligned} \tag{22}$$

where $L_1 = \log(M_w/M_n)$ and $L_2 = \log(M_z/M_w)$.

MWD from dynamic moduli data

The methodology illustrated so far has been applied to various polymers. A polyacetal sample, Celcon M25 (Nobile and Cocchini 1999), a polypropylene P3 sample (Wasserman and Graessley 1996), and the two mixtures M1 and M2, obtained by mixing nearly monodisperse polystyrenes (Wasserman and Graessley 1992) have been analyzed.

The material parameters for the various polydisperse samples are those reported in the referenced papers (or obtained from information reported therein) and they are recalled in Table 1. In the case of the zero-shear rate viscosity, the experimental values are reported.

Analogously, the molecular weight averages of the Celcon M25 and of the P3 samples as obtained from GPC measurements have been recalled in Table 2. In the same table the molecular weight averages for the M1 and M2 mixtures calculated from the known composition of the mixture (Wasserman and Graessley 1992) are also reported.

The fitting procedure has been applied to the dynamic moduli data by minimizing the χ^2, only as a function of the a and b parameters of the GEX distribution. The other parameters (k, α, M_0, and G_N^0) are either those reported in Table 1 or have been evaluated by using the constraints discussed above. Indeed, for all the polymers tested, the k and α parameters are those from Table 1. For what concerns the G_N^0 values, in the case of the M25, P3, and M1 mixture, they have been calculated by using the constraint of Eq. (21), and they are reported in Table 3. In particular, for the M1 mixture a G_N^0 value of 1.9×10^5 Pa is obtained, that compares well with the value of 2×10^5 Pa from the literature (Table 1). For comparison, the fitting procedure has also been performed with this last value, obtaining quite comparable results. Therefore, in the case of the M2 mixture, the value from the literature has directly been used.

For the sake of the discussion, it is worth mentioning that in the case of isotactic polypropylene, plateau modulus data for narrow fractions are not reported in literature. The value of 4.5×10^5 Pa, reported in Table 1, refers to the plateau value for atactic polypropylene as first evaluated by Plazek and Plazek (1983) and by Fetters et al. (1994), and later used by Wasserman and Graessley (1996) in the discussion of their experimental results on P3. It corresponds to an entanglement molecular weight $M_e = 6520$. Therefore, following this suggestion in the analysis of the moduli data of P3 by the fitting to our model, we first used the value proposed for the atactic – PP. The results obtained in terms of the molecular weight averages, also reported in Table 3, however, are in significant disagreement with the corresponding values reported from GPC. Somewhat better agreement with the GPC data has been obtained by using the constraint of Eq. (21), obtaining a G_N^0 value of 3×10^5 Pa. To confirm this result, the Wu relationship (Eq. 20) has also been used, and a similar estimate for G_N^0 has been obtained, even if the polydispersity index for P3, $p = 4.7$, is beyond the ascertained range of validity of Eq. (20). On the other hand, neither the sum-rule, Eq. (19), nor the tan δ minimum criterion could be applied to the P3 data in the frequency range available.

Table 2 Molecular weight averages for the same polymer samples as in Table 1 obtained from GPC measurements (Celcon M25 and P3) and from calculation on the known composition of the mixtures (M1 and M2)

Sample	M_n	M_w	M_z	M_{z+1}
Polyacetal M25	53,000	109,000	183,000	
Mixture M1	154,000	356,000	670,000	1,300,000
Mixture M2	155,000	398,000	1,040,000	2,450,000
Polypropylene P3	65,000	360,000	1,040,000	1,880,000

Finally, the τ parameter has been calculated from Eq. (18) with the experimental values of the zero shear-rate viscosity as reported in Table 1. The corresponding values have been reported in Table 3. As indicated in Eq. (8), the τ values will give the M_0 parameters.

The results of the fitting procedure on the dynamic moduli data have been reported in Figs 4, 5, 6, and 7 and summarized in Table 3.

The range of dynamic moduli data actually used in the fitting procedure has been indicated with arrows in the figures. Figures 4, 5, 6, and 7 show that the fit is generally satisfactory. Some discrepancy between the predicted and experimental G′ values is observed at the low frequencies, where a less accurate prediction of the model is expected.

Table 1 Material parameters for the polyacetal sample Celcon M25 (Nobile and Cocchini 1999), the polypropylene P3 sample (Wasserman and Graessley 1996), and the two polystyrene mixtures M1 and M2 (Wasserman and Graessley 1992)

Sample	T (°C)	η_0 (Pa s)	k	α	G_N^0 (Pa)
Polyacetal M25	190	3870	8.54×10^{-15}	3.50	NA
Mixture M1	150	8.00×10^6	1.68×10^{-12}	3.38	2×10^5
Mixture M2	150	1.64×10^7	1.68×10^{-12}	3.38	2×10^5
Polypropylene P3	190	11,025	5.32×10^{-17}	3.60	4.5×10^5

Table 3 Results of the fitting procedure on the polymer samples. The value of G_N^0 reported in the table are those obtained by using the constraint of Eq. (21)

Sample	G_N^0 (Pa)	τ (s)	a	b	M_n	M_w	M_z	M_{z+1}
M25	1.47×10^6	5.28×10^{-10}	2.26	0.46	57,000	118,000	204,000	316,000
M1	From Table 1	2.88×10^{-2}	0.59	0.55	74,000	340,000	763,000	1,330,000
	1.9×10^5	8.81×10^{-1}	0.34	0.69	59,000	324,000	684,000	1,115,000
M2	From Table 1	1.43×10^{-3}	0.88	0.47	107,000	422,000	961,000	1,737,000
P3	From Table 1	2.31×10^{-8}	0.36	0.37	36,000	494,000	1,756,000	4,120,000
	3.0×10^5	9.61×10^{-8}	0.59	0.43	62,000	399,000	1,102,000	2,228,000

The molecular weight averages reported in Table 3 have been obtained from Eq. (3) with the best-fit a and b parameters and with M_0 evaluated from Eq. (8). The 90% confidence intervals are nearly ±10%, ±1%, ±1%, and ±3% for M_n, M_w, M_z, and M_{z+1} for all samples tested.

The molecular weight averages reported in Tables 2 and 3 are in a fairly good agreement, except the case of P3

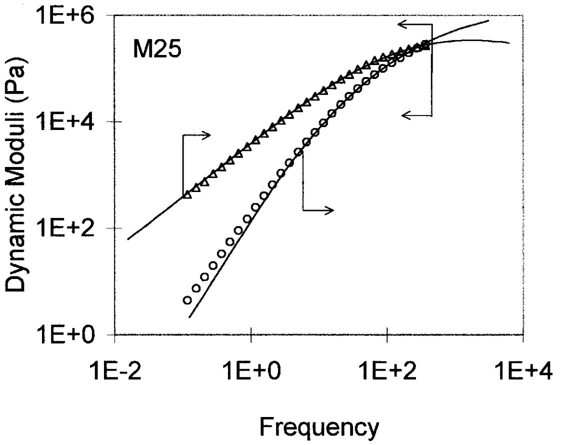

Fig. 4 Dynamic data, G′ (○) and G″ (△), for the polyacetal Celcon M25 at $T_0 = 190$ °C (Nobile and Cocchini 1999). The *continuous curves* are the fit with the GEX-double reptation model for dynamic moduli, Eqs. (7) and (12). The *arrows* give the frequency range actually used for fitting

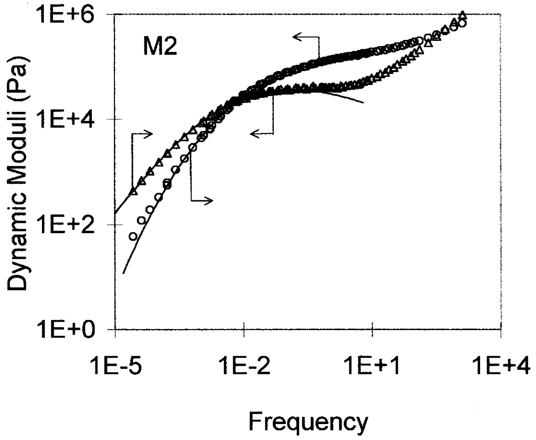

Fig. 6 Dynamic data, G′ (○) and G″ (△), for the polystyrene mixture M2 at $T_0 = 150$ °C (Wasserman and Graessley 1992). The *continuous curves* are the fit with the GEX-double reptation model for dynamic moduli, Eqs. (7) and (12). The *arrows* give the frequency range actually used for fitting

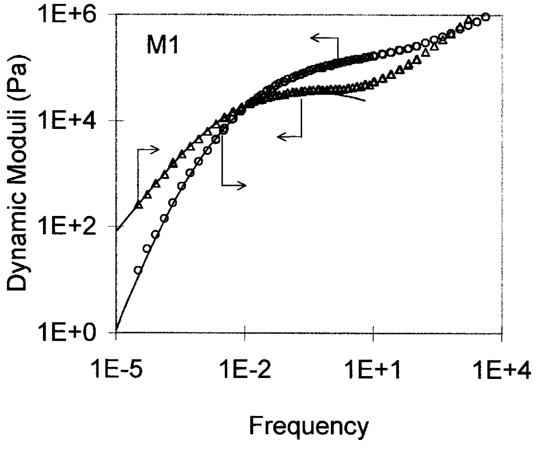

Fig. 5 Dynamic data, G′ (○) and G″ (△), for the polystyrene mixture M1 at $T_0 = 150$ °C (Wasserman and Graessley 1992). The *continuous curves* are the fit with the GEX-double reptation model for dynamic moduli, Eqs. (7) and (12). The *arrows* give the frequency range actually used for fitting

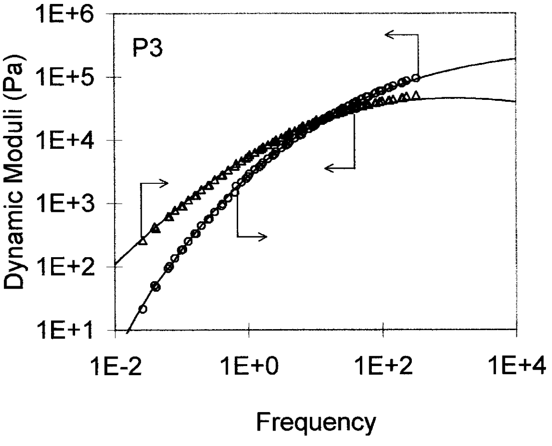

Fig. 7 Dynamic data, G′ (○) and G″ (Δ), for the polypropylene P3 sample at $T_0 = 190$ °C (Wasserman and Graessley 1996). The *continuous curves* are the fit with the GEX-double reptation model for dynamic moduli, Eqs. (7) and (12). The *arrows* give the frequency range actually used for fitting

with the G_N^0 value from the literature, as already discussed previously. Concerning the M_w and M_z values, the predictions obtained from the dynamic moduli measurements, Table 3, differ by less than 10% with respect to those obtained either from GPC measurements (Celcon M25 and P3) or from the knowledge of the composition (M1 and M2 mixtures), Table 2. The discrepancies increase at about 20% for M_{z+1}. In particular, the procedure satisfactorily catches the differences between the M1 and M2 mixtures, which differ in their composition only at the high molecular weight tail.

More controversial results are obtained for M_n. In the case of M25 and P3 samples, the predictions for M_n differ by less than 10% from the corresponding values obtained by GPC measurements, while for the two polystyrene mixtures they differ by more than 50% from the corresponding values obtained by calculation from the known composition of the mixtures. This event could be justified by the low sensitiveness of the rheological measurements on the M_w/M_n ratio, as shown in Fig. 3.

Conclusions

In this paper the analytical solution for the relaxation modulus from the double reptation model with the Tuminello step relaxation function and the GEX MWD function has been used to obtain MWD from viscoelastic data. The model obtained so far has been, in fact, applied to get the MWD of different polymers from their dynamic data by least-squares fitting, *without the need for the inversion* of the double reptation integral equation. Moreover, to evaluate the dynamic moduli from the relaxation ones in an efficient and accurate numerical way, a Finite Element Approximation (FEA) technique has been used. The sensitiveness of the GEX-double reptation dynamic moduli on the model parameters has been investigated and the results have shown that the evaluation of the MWD from rheological data will provide well defined M_z/M_w ratios, while the M_w/M_n ratios will have large confidence intervals. Finally, concerning the M_w and M_z values, the predictions obtained from the dynamic moduli measurements differ less than 10% from those obtained from GPC measurements, while, as expected, more uncertainty is present in the M_n predictions.

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