

Relaxation spectra of binary blends: Extension of the Doi-Edwards theory

M. A. TCHESNOKOV¹, J. MOLENAAR², J. J. M. SLOT^{3,4} and R. STEPANYAN⁴

¹ *Department of Applied Mathematics, University of Twente - PO Box 217, 7500 AE Enschede, The Netherlands*

² *Wageningen University, Department of Mathematics & Biometris - PO Box 100, 6700 AC Wageningen, The Netherlands*

³ *Eindhoven University of Technology, Faculty of Mathematics and Computer Science PO Box 513, 5600 MB, Eindhoven, The Netherlands*

⁴ *DSM Research, Material Science Centre - PO Box 18, 6160 MD Geleen, The Netherlands*

received 19 April 2007; accepted in final form 9 August 2007
published online 5 September 2007

PACS 61.25.Hg – Macromolecular and polymer solutions; polymer melts; swelling
PACS 83.10.Kn – Reptation and tube theories
PACS 83.60.Bc – Linear viscoelasticity

Abstract – A molecular model is presented which allows the calculation of the stress relaxation function G for binary blends consisting of two monodisperse samples with arbitrary molecular weights. It extends the Doi-Edwards reptation theory (DOI M. and EDWARDS S. F., *The Theory of Polymer Dynamics* (Oxford Press, New York) 1986) to highly polydisperse melts by including constraint release (CR) and thermal fluctuations (CLF), yet making use of the same input parameters. The model reveals an explicit nonlinear dependence of CR frequency in the blend on the blend's molecular weight distribution (MWD). It provides an alternative way to quantify polydisperse systems compared to the widely used "double-reptation" theories. The results of the present model are in a good agreement with the experimental data given in RUBINSTEIN M. and COLBY R. H., *J. Chem. Phys.*, **89** (1988) 5291.

Copyright © EPLA, 2007

The molecular model of Doi and Edwards (DE) [1] proved to be remarkably successful in predicting the rheological response of linear monodisperse polymer melts in the linear viscoelastic regime. Some initial shortcomings in this regime could be eliminated by including a rigorous treatment of thermal fluctuations [2]. However, already in an early stage it was realized that its straightforward extensions to polydisperse systems, such as binary blends, did not adequately describe the observed rheological behavior [3]. This discrepancy between theory and experiment strongly suggested that the fundamental postulate of the DE model that the surrounding network of polymers constitutes a time-independent mean field of topological constraints is not applicable in case of polydisperse materials. It breaks down because a low molecular weight polymer imposing a constraint on a high molecular weight test chain can diffuse away much faster than the test chain reptates. Clearly, any realistic model for polydisperse systems must provide a rigorous treatment of constraint release along with thermal fluctuations.

In a number of attempts one has tried to adjust the original DE model through inclusion of constraint release [4–7]. Most of these extensions led to models, that were mathematically complicated and still had restricted predictive capability and thus limited practical utility. Alternatively to the DE theory, des Cloizeaux and Tsenoglou independently developed a network model [8,9] for linear viscoelastic materials based on the concept of "double reptation". Their formalism allows one to express the stress relaxation function of a polydisperse melt in terms of relaxation spectra of each of its monodisperse components and a so-called "mixing rule". Double reptation theory shows a good agreement with observed data on polydisperse melts with rather narrow molecular weight distribution (MWD). The broader the MWD, the larger the disagreement between theoretical predictions and data. Recently, Mead [10] extended the "double reptation" theory to non-linear flows by introducing convective constraint release and stretch in the model.

In this paper we develop a molecular model for binary blends which consist of two monodisperse components with arbitrary molecular weights (but larger than the critical entanglement weight M_c). The MWD of these melts has a distinct two-peaked structure. The model extends the original Doi-Edwards formalism to incorporate CR and thermal fluctuations, yet has the same input parameters as the original DE model.

A binary blend consists of long and short polymers with molecular weights M_l and M_s , respectively. In the following they will be referred to as l - and s -polymers. Following the tube concept [1], the motion of a polymer in the melt is represented by the motion of its primitive chain. So, “polymer” and “primitive chain” will be used interchangeably in the text.

In the linear viscoelastic regime, polymers in the blend are hardly stretched. The position of each segment of a polymer can then be described by its curvilinear coordinate s_0 , measured along the primitive chain from the center to the segment. The equilibrium lengths of the primitive chains of l and s polymers are denoted by L_{l0} and L_{s0} , respectively. The center of the polymer corresponds to $s_0 = 0$ and the endpoints to $s_0 = \pm L_0/2$.

In the absence of CR, the Brownian motion of a polymer in the melt implies its one-dimensional diffusion inside the tube, called reptation. Due to reptation, the chain vacates the original tube (tube at time $t = 0$) at the endpoints. As soon as a part of the tube is vacated, it disappears, leading to a gradual shortening of the original tube and thus relaxation of the original configuration. According to the DE theory, the stress induced in the material is directly related to the amount of orientation in the tubes. Randomization of tubes via reptation therefore leads to stress relaxation.

Inclusion of CR in this picture allows the polymer chain to make random local (lateral) jumps and so enhances the rate at which the initial tube is relaxed. CR leads to lateral diffusion of the polymer through the entanglement network. This motion is different from reptation which is diffusion along the tube. Let ν_i be the CR frequency on i -chains ($i = l, s$) and a_0 the mean equilibrium distance between entanglements. Since each jump is over a distance order of a_0 , the CR diffusion coefficient for i -chains can be estimated as $D_{iCR} = \nu_i a_0^2$. Since constraint release works independently of reptation, the overall diffusion coefficient is then the sum $D_{iREP} + D_{iCR}$, where D_{iREP} is the reptation diffusion coefficient for i -polymers.

Gradual renewal of the initial tube is normally described by the tube survival probability $G(s_0, t)$, the average probability for segment s_0 of the initial tube to have survived at time t . As was shown by Doi and Edwards [1], if $G(s_0, t)$ is known, one can easily calculate the rheological response of the melt to a given deformation history. The equation of motion for $G_i(s_0, t)$ of i -polymers in the presence of CR has the form

$$\frac{\partial G_i}{\partial t} = \left[D_{iREP} + \nu_i a_0^2 \right] \frac{\partial^2 G_i}{\partial s_0^2}. \quad (1)$$

In the absence of CR, eq. (1) boils down to the well-known equation of Doi and Edwards. It shows that inclusion of CR into the DE theory effectively amounts to a decrease of the terminal reptation time T_{iREP} ($T_{iREP} \propto D_{iREP}^{-1}$) by a factor of $(1 + \nu_i a_0^2 / D_{iREP})$. From eq. (1) we see that the reciprocal relaxation time due to CR necessary to renew the entire tube is of order ν_i / Z_i^2 with $Z_i \approx L_{i0} / a_0$ the number of tube segments. A similar result follows from the well-known Verdier-Stockmayer “bond-flip” model for CR [11].

In contrast to earlier extensions of the DE theory [4–7] and double reptation theories [8–10], the present model does not assume that in general the stress relaxation function of i -polymers (which is proportional to the fraction of the initial tube survived at time t), cannot be presented as the product of a pure “reptational” and a “constraint release” part. In fact, as is seen from eq. (1), this assumption only works if one neglects higher-order CR relaxation modes in the polymer dynamics, which can only be justified for very long polymers. In this paper we do not restrict the molecular weights of the blend’s components, and so we have to solve the “full” equation, eq. (1).

To complete eq. (1), we must specify the ν_i coefficients. In a binary blend, two types of polymers entangle with each other, so we meet with two sorts of constraints. Constraints of the j -th sort (j -constraints for short) are imposed by j -polymers. Their mean life-time τ_j depends on the molecular parameters of the j -polymers. If $\phi_j^{(i)}$ is the mean fraction of j -constraints per i -chain, then the characteristic CR frequency ν_i of the i -polymers is given by

$$\nu_i = \sum_{j=L,S} \frac{1}{\tau_j} \phi_j^{(i)}. \quad (2)$$

To calculate $\phi_j^{(i)}$ ($i, j = l, s$), let us assume that all the entanglements in the blend are pair-wise contacts between polymers. Then, the entanglement network in the blend can be considered as consisting of interacting “half-entanglements”, which are either of s or of l type. Each entanglement is built up out of two half-entanglements and is thus of one of three possible types: ll , ls , and ss . If Z_i is the mean number of constraints per i -polymer, then each i -polymer contributes to Z_i half-entanglements of the i -th sort.

Let W_i be the fraction of i -half-entanglements per unit volume in the melt. If n_i is the concentration of i -polymers in the melt, then the concentration of i -half-entanglements is $n_i M_i / M_e$ with M_e the mean molecular weight between entanglements. Since the overall concentration of half-entanglements is $2/a_0^3$, we have

$$W_i = \frac{\rho a_0^3}{2M_e} \omega_i, \quad i = l, s. \quad (3)$$

Here $\omega_i = n_i M_i / \rho$ is the mass fraction of i -chains, and ρ the blend density. The fractions ω_l and ω_s represent the molecular weight distribution (MWD) of the blend. Note

that this distribution is normalized, *i.e.* $\omega_l + \omega_s = 1$. Note that $\rho a_0^3 / M_e$ is order of the mean number of polymers that constitute one entanglement. Here we assume it is two and therefore $W_i \simeq \omega_i$.

If we assume that the half-entanglements are homogeneously distributed over the melt, the corresponding volume fractions of entanglements of each sort are given by

$$W_{ii} = W_i W_i, \quad W_{i \neq j} = 2W_i W_j, \quad (4)$$

where the prefactor 2 in the expression for W_{ij} is due to the fact that $W_{ij} = W_{ji}$. In terms of fractions W_{ij} , the CR matrix $\phi_j^{(i)}$ has the form

$$\phi_j^{(i)} = \frac{W_{ij}}{W_{is} + W_{il}}. \quad (5)$$

Substitution of eq. (3) and eq. (4) into eq. (5) therefore yields

$$\phi_i^{(i)} = \frac{\omega_i}{2 - \omega_i}, \quad \phi_{j \neq i}^{(i)} = \frac{2\omega_j}{2 - \omega_i}. \quad (6)$$

Equations (6) reveals that the factors $\phi_j^{(i)}$ are only functions of the MWD. An important finding from eqs. (6) is that their dependence on the MWD is non-linear. However, in theories for polydisperse systems, these fractions are normally assumed to be proportional to the weight fractions of corresponding polymers. The presence of non-diagonal components $\phi_{j \neq i}^{(i)}$ mirrors that the motions of different sorts of polymers in the blend are coupled. Clearly, the stress relaxation function of the blend cannot be expressed via a linear combination of the corresponding ‘‘monodisperse’’ functions of its components.

Now let us find the mean life-time τ_j of j -constraints in eq. (2), which amounts to calculation of the mean life-time of j -half-entanglements. In general, each of these half-entanglements is ‘‘destroyed’’ by either reptation or retraction of j -chains. In this paper, as mentioned above, we restrict ourselves to the linear viscoelastic regime which corresponds to flow rates $\dot{\gamma} \ll T_{LRouse}^{-1}$, where T_{LRouse}^{-1} is the Rouse time of long molecules. In this regime, the half-entanglements are mostly destroyed by reptation and so release of constraints due to retraction can be neglected.

Let δt_j be the time needed for j -chains to reptate over a distance a_0 inside their tubes. In the absence of contour length fluctuations, reptation of a j -chain during the time interval from 0 to δt_j will release (on average) one constraint on another chain, or, in other words, will ‘‘destroy’’ two half-entanglements. These half-entanglements may be of different kind. The probability to destroy one i - and one j -half-entanglement equals $W_{i \neq j}$, whereas in case of two j -half-entanglements this probability is given by W_{jj} . Let us denote the concentration of j -half-entanglements at time t as $N_j(t)$, then its decrease in the time interval δt_j is given by

$$N_j(\delta t_j) - N_j(0) = -n_j(W_{ij} + 2W_{jj}). \quad (7)$$

Of course, also new half-entanglements are created in this time interval, but they do not contribute to the stress, since their conformation is random. That is why they are not taken into account here. In eq. (7), n_j is the concentration of j -polymers in the melt and $N_j(t=0) = n_j Z_j$ is the number of j -half-entanglements at time $t=0$. On the other hand, if τ_j is the mean-life time of j -half-entanglements, then

$$N_j(t) = N_j(0) \cdot e^{-t/\tau_j} \quad (8)$$

From eq. (7) and eq. (8) and the fact that $\delta t_j \approx a_0^2 / 2D_{jREP}$ we find that

$$\tau_j \approx \frac{Z_j}{W_{ij} + 2W_{jj}} \frac{a_0^2}{2D_{jREP}}. \quad (9)$$

Since fractions W_{ij} are functions of the MWD, it follows from eq. (9) that the mean life-time of j -constraints is not only a function of the molecular parameters of the j -polymers, but also depends on the MWD. Constraint release in the blend exhibits a complex non-linear MWD dependence.

Application of eqs. (6) and eq. (9) to a monodisperse melt yields the insight that the diffusion coefficient due to CR in eq. (1) is Z times smaller than the one due to reptation. That is why CR plays only a minor role in the dynamics of monodisperse melts and the original Doi-Edwards theory applies. A similar conclusion holds for polydisperse melts that consist of components with nearly equal molecular weights. However, in highly polydisperse melts, CR is mainly driven by diffusion of the short chains. Then, it plays a significant role in the melt dynamics and its proper treatment becomes crucial in any realistic model for the rheological behavior of the blend.

So far, we have ignored contour length fluctuations (CLF). This alternative relaxation mode stems from the fast ‘‘inwards’’ and ‘‘outwards’’ motions of the *physical* chain’s end at the tube ends, which leads to a shortening of the tube survival time. The importance of CLF in relaxation spectra of linear polymers was recognized by Milner and McLeish [2] who showed that inclusion of CLF into the reptation yields the correct power law $\omega^{-1/4}$ dependence of the dynamic loss modulus $G''(\omega)$ at high frequencies. To include CLF in our model, we introduce the dimensionless variable $x_i = 1 - 2s_0/L_{i0}$, which gives a fractional distance from tube segment s_0 to the chain end ($s_0 > 0$). According to [2], the average relaxation time $\tau_i(s_0)$ of tube segment s_0 of an i -chain due to CLF is given by

$$\tau_i(x_i) \approx \begin{cases} \tau_e Z_i^4 x_i^4, & x_i \ll x_i^*, \\ \tau_e x_i^{-1} Z_i^{3/2} e^{0.75 Z_i x_i^2}, & x_i > x_i^*, \end{cases} \quad (10)$$

where τ_e is the Rouse time [1] of one entanglement segment and $x_i^* = C/\sqrt{Z_i}$, where C is a numerical coefficient of

order unity. Numerical simulations of CLF reported in [12] gave $C \approx 1.5$ (taking into account the difference in the notations). Equation (10) shows that $\tau_i(x)$ starts to grow rapidly with x_i near x_i^* . Clearly, for linear polymers CLF mostly govern the relaxation of those tube segments for which $x_i < x_i^*$. So, this effect controls the relaxation spectrum of each blend component at frequencies $\omega > 1/\tau_e Z_i^2$. To interpolate between the so-called breathing regime with $x_i \ll x_i^*$ and the activation regime with $x_i > x_i^*$, we use the exponential interpolation formula

$$\frac{\tau_i}{\tau_e} = e^{-x_i/x_i^*} Z_i^4 x_i^4 + (1 - e^{-x_i/x_i^*}) x_i^{-1} Z_i^{3/2} e^{0.75 Z_i x_i^2}. \quad (11)$$

Inclusion of CLF into eq. (1) yields that the stress relaxation function $G_i(t)$ of the i -th component is a solution of

$$\frac{\partial G_i}{\partial t} = \left[D_{iREP} + \nu_i^* a_0^2 \right] \frac{\partial^2 G_i}{\partial s_0^2} - \frac{1}{\tau_i} G_i. \quad (12)$$

Equation (12) lies at the heart of our model. It includes all relevant relaxation modes, *i.e.*, reptation, CR, and CLF. Since both CR and CLF become unimportant for very long polymers, eq. (12) boils down to the theory of DE in the limit $Z_i \rightarrow \infty$. Due to constant coefficients, eq. (12) can readily be rewritten in terms of (ω, s_0) coordinates to ease the calculation of the blend's storage and loss moduli. In the absence of CR, eq. (12) reduces to the result developed in [13], which holds for the linear viscoelastic regime. Note that CLF leads to an effective increase in D_{iREP} by a factor of $1/(1 - x_i^*)^2$ (see [1]); this is in agreement with the interpretation that CLF enhance the diffusion of a chain inside its tube. Since enhanced reptation leads to enhanced CR, appropriate changes should be made in eq. (9).

To solve eq. (12), we need the initial and boundary conditions for $G_i(s_0, t)$. Clearly, $G_i(s_0, 0) = 1$ for all s_0 along the tube. Due to CLF the chain ends fastly move inward and outward over short distances. This implies an instantaneous relaxation of tube segments at $s_0 = \pm L_{i0}/2$, and hence

$$G_i(\pm L_{i0}/2, t) = 0. \quad (13)$$

In terms of $G_i(s_0, t)$ the stress relaxation function $G(t)$ of the blend has the form [1]

$$G(t) = \sum_{i=l,s} \omega_i G_i(t), \quad G_i(t) = \frac{G_{i0}}{L_{i0}} \int_{-L_{i0}/2}^{L_{i0}/2} G_i(s_0, t) ds_0, \quad (14)$$

where G_{i0} is the elastic modulus of i -polymers.

In the absence of CR, $G_i(t)$ is a function of the molecular parameters of i -polymers only. Then, $G(t)$ depends linearly on the MWD and $G(t)$ is equal to the "monodisperse" relaxation function $G_i(t)$ averaged over the blend's MWD. In the presence of CR, $G_i(t)$ depends nonlinearly on the MWD via ν_i .

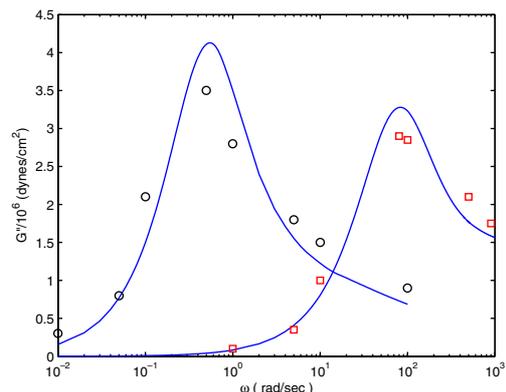


Fig. 1: Simultaneous fit of loss moduli for the two monodisperse PBd samples. Lines are the fitting results; points are the data: open circles are data for $M = 355000$, open squares are data for $M = 70900$.

This implies that in general $G(t)$ cannot be expressed in terms of the relaxation spectrum of a monodisperse melt in combination with a mixing rule, as assumed in molecular theories based on the "double reptation" picture. The deviation from the linear law reported for various polydisperse systems (*e.g.*, Rubinstein and Colby [4]) is clearly due to pronounced constraint release.

As mentioned earlier, the presented model can be reduced to the previous extensions of the DE theory for blends if one neglects high order CR modes in eq. (12). These extensions showed a good agreement with experimental data for blends with narrow MWD [14,15], whilst for blends where components have very different molecular weights the agreement was only satisfactory. To show that the presented model is able to describe the rheological response of a highly polydisperse melt, the model predictions will be compared with the data of Rubinstein and Colby [4]. They used a binary blend consisting of two monodisperse polybutadiene (PBd) samples with molecular weights $M_s = 70900$ and $M_l = 355000$. The reported entanglement molecular weight M_e for PBd is 1815 [16]. The mean number of constraints are estimated to be 195 and 40 for the long and short chains, respectively. The elastic moduli $G_{l0} = G_{s0} = G_0$ and reptation times are obtained by simultaneous fitting the loss modulus $G''(\omega)$ of two monodisperse PBd melts (with the molecular weights mentioned above). The results of this fitting are shown in fig. 1.

The best fit is obtained for $G_0 = 1.2$ MPa, $T_{sREP} = 0.025$ s, and $T_{lREP} = 3.0$ s. The estimated for G_0 is in good agreement with the experimentally measured $G_0 = 1.25$ MPa [16]. Note that $T_{sREP}/T_{lREP} = M_s^3/M_l^3$, as expected [1]. Given the molecular parameters of the components of the blend, the model is able to predict its linear rheological response quantitatively. In fig. 2, the model predictions are compared with the data from [4] for two blend compositions: $\phi_l = 0.882$ and $\phi_l = 0.768$ (ϕ_l is the volume fraction of long chains). As is seen, the

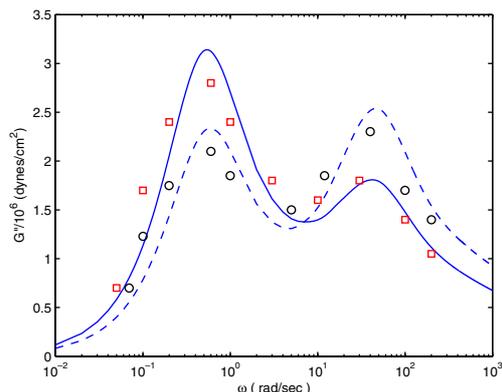


Fig. 2: Comparison of blend predictions with data for two blend compositions. Solid line is the prediction, and open squares are the data for $\phi_l = 0.882$. Dashed line and open circles for $\phi_l = 0.768$.

model reproduces the two-peaked structure of the blend relaxation spectrum quite well.

In conclusion, our molecular model yields the linear rheological response of a binary blend without any restriction on the peak positions in the MWD and leads to a very good agreement between measurements and predicted values. This is apparently so thanks to the accurate treatment of CR. The derivation of the present model reveals that the mean-life time of a constraint imposed by one chain on another is a nonlinear function of the MWD, which indicates that the application of so-called “mixing rules” can only have limited relevance. The present model is especially relevant for highly polydisperse systems. Finally, we would like to emphasize that the theory presented here can easily be extended to systems with arbitrary number of components or even continuous MWD, and thus may have a great practical utility.

This research is supported by the Technology Foundation STW, applied science division of NWO, and the technology programme of the Ministry of Economic Affairs of the Netherlands.

REFERENCES

- [1] DOI M. and EDWARDS S. F., *The Theory of Polymer Dynamics* (Oxford Press, New York) 1986.
- [2] MILNER S. T. and MCLEISH T. C. B., *Phys. Rev. Lett.*, **81** (1998) 725.
- [3] STRUGLINSKI M. J. and GRAESSLEY W. W., *Macromolecules*, **18** (1985) 2630.
- [4] RUBINSTEIN M. and COLBY R. H., *J. Chem. Phys.*, **89** (1988) 5291.
- [5] GRAESSLEY W. W. and STRUGLINSKI M. J., *Macromolecules*, **19** (1986) 1754.
- [6] DOI M., GRAESSLEY W. W., HELFAND E. and PEARSON D. S., *Macromolecules*, **20** (1987) 1900.
- [7] GRAHAM R. S., LIKHTMAN A. E. and MCLEISH T. C. B., *J. Rheol.*, **47** (2003) 1171.
- [8] DES CLOIZEAUX J., *Macromolecules*, **23** (1990) 4678.
- [9] TSENOGLOU C., *Macromolecules*, **24** (1991) 1762.
- [10] MEAD D. W., *Rheol. Acta*, **46** (2007) 369.
- [11] VERDIER P. H. and STOCKMAYER W. H., *J. Chem. Phys.*, **36** (1962) 227.
- [12] LIKHTMAN A. E. and MCLEISH T. C. B., *J. Chem. Phys.*, **35** (2002) 6332.
- [13] MEAD D. W., LARSON R. G. and DOI M., *Macromolecules*, **31** (1998) 7895.
- [14] WATANABE H. and KOTAKA, *Macromolecules*, **17** (1984) 2316.
- [15] WATANABE H., SAKAMOTO T. and KOTAKA T., *Macromolecules*, **18** (1985) 1008.
- [16] FETTERS L., LOHSE D. J., RICHTER D., WITTEN T. A. and ZIRKEL A., *Macromolecules*, **27** (1994) 4639.