

# ESTIMATION OF THE MOLECULAR WEIGHT DISTRIBUTION OF LINEAR HOMOPOLYMER BLENDS FROM LINEAR VISCOELASTICITY FOR BIMODAL AND HIGH POLYDISPERSE SAMPLES

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**Abstract--** This work is concerned with the approximate solution of the problem generated by the integral of first kind relating the shear relaxation modulus of entangled, linear and flexible homopolymer blends and the molecular weight distribution (MWD). Procedures are proposed to estimate the density distribution function (DDF) of the MWD from numerical solutions of the theoretical model composed by the double reptation mixing rule and a law for the relaxation time of chains in polydisperse matrixes. One procedure uses the expansion of the DDF through orthogonal polynomial functions. This expansion is formulated for two cases: a) Hermite polynomials associated with the normal-DDF and b) Laguerre polynomials associated with the gamma-DDF. The other procedure uses the mean value theorem of continuum functions, which turns out the integral problem into a differential form. Calculations are carried out with dynamic rheometric data of linear viscoelasticity for samples of polydimethylsiloxane, polypropylene and polybutadiene. High values of polydispersity are considered. The predictions of the DDF through these procedures compare well with experimental data of size exclusion chromatography (SEC).

**Keywords--** Bimodal Molecular Weight Distribution, High Polydispersity, Hermite and Laguerre Series, Double Reptation Model, Linear Flexible Homopolymer Blends.

## I. INTRODUCTION

The relation between the linear viscoelastic functions and the molecular weight distribution (MWD) involving linear and flexible homopolymer blends is a subject of intensive research at present, because several theoretical and numerical aspects must be still elucidated. This work considers one aspect, which consists on finding an approximate solution for the density distribution function (DDF)  $f_w(M)$  from the double reptation-mixing rule (Tsenoglou, 1991; des Cloizeaux, 1990a, 1990b and 1992) where data of the relaxation modulus  $G(t)$  are required. This problem is ill-posed in the sense

that many solutions of the DDF can be found satisfying this mixing rule expressed through an integral of first kind (see, for example, de Hoog, 1980 and Baker, 1977). From a practical point of view, one has to observe that the processability of polymeric compounds and the mechanical properties of final crosslinked products are significantly affected by the macromolecular statistics. Therefore, the knowledge of the DDF of a polymeric network obtained via dynamic rheometry can be useful as far as one can choose the physical solution from many ones available from this method of determination.

In this section, we define first the problem found in the determination of the DDF from dynamic rheometry, to propose then procedures for its numerical evaluation. The theoretical model is basically composed by the double reptation mixing rule (see also Anderssen and Mead, 1998),

$$\sqrt{\frac{G(t)}{G_N^o}} = \int_{\ln M_c}^{\infty} [\sqrt{f(t, \lambda)}]_{\lambda=\lambda(M)} f_w(M) d \ln M \quad (1)$$

and a relaxation law  $\lambda = \lambda(M, f_w(M)) \equiv \lambda(M)$  for the maximum relaxation time  $\lambda$  of a monodisperse fraction expressed as function of both  $M$  and DDF. In Eqn. (1),  $G_N^o$  is the plateau modulus of the blend. In addition, the relaxation modulus of the flexible, linear and monodisperse polymer is designated  $g(t, \lambda)$ , and the reduced relaxation function  $f(t, \lambda)$  is approximated by a single exponential as follows,

$$\sqrt{f(t, \lambda)} = \left( \frac{g(t, \lambda)}{g_N^o} \right)^{\frac{1}{2}} = \exp \left\{ -\frac{t}{2\lambda} \right\} \quad (2)$$

where  $g_N^o$  is the rubbery plateau value of the monodisperse fraction that is independent of the molecular weight  $M_w$  when  $Po=1$  and for an ideal network where  $M_c/M_n \ll 1$ . The critical molecular weight required to form a network is  $M_c = 2M_e$ , and hence,  $f_w(M)=0$  for  $M < M_c$  is a constrain of the DDF. Also,  $M_e = \rho RT/G_N^o$  is the average molecular weight between entanglements,  $\rho$  is the polymer