

Some applications of molecular rheology: Polymer formulation and molecular design

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Abstract

“Molecular rheology” is the missing link between the macromolecular structure of polymeric materials and their viscoelastic properties in the melt state. It complements the engineering or continuum mechanics aspects of rheology, which generally ignores the molecular details of the objects under study. The pioneering vision of the diffusion and relaxation processes of flexible macromolecular chains initiated by P.-G. de Gennes has led to very effective and predictive models of viscoelasticity of polymer melts, which go far beyond academic interest.

We present, in this paper, two very different examples of application of molecular rheology: molecular design of block copolymers corresponding to expected end-user properties (which are directly linked to linear viscoelastic properties) and formulation of blends of linear polymers in order to get strain-hardening effects in non-linear viscoelasticity usually obtained with long-chain branched (LCB) materials. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Many studies [1–4] have focused on the rheological properties of polymer melts in elongational flow situations. A key feature for a good processability of thermoplastics is the strain-hardening (SH) effect in elongation which is specific of long-chain branched (LCB) materials. A small amount of LCB material may improve a given process (such as bubble stability in film blowing) or be catastrophic (accidental tail of LCB material in applications for linear polyolefins). In the first case, “intelligent” polymer formulation may improve considerably the processability of materials. “Molecular rheology” may lead to predictive formulation by inverting molecular models of viscoelasticity. Furthermore, these models demonstrate that it is possible to get strain-hardening effects by blending species of low/high molecular weight linear materials following specific rules as far as concentrations and molecular weights are concerned. This feature has indeed been observed experimentally, in particular by

Minegishi et al. [5] who have studied the effect of an ultra high molecular weight tail on the flow properties of binary blends of linear polystyrene. We have performed complementary studies and will focus on the molecular aspects and modeling of the data. As the occurrence of strain hardening may be predicted from molecular considerations, this opens the way to predictive formulation of polymers (mainly polyolefins).

Another and different example of practical application of molecular rheology will be presented. The thermorheological properties of hot-melt pressure sensitive adhesives (HMPSA) govern in a large extent their process behavior (blending, flow properties, pelletizing and die-cutting for label applications) as well as their end-user properties (tack, adherence and shear resistance) [6,7]. In most aspects, rheological (i.e. viscoelastic) parameters may be associated with processing ability, application end-user properties. Typical industrial applications for HMPSAs described in this paper are labels and tapes. Hot-melt formulations are basically made of two components: a polymer base which brings cohesion as well as good mechanical properties, and a tackifying resin which gives expected tack properties to the adhesive and governs the thermorheological properties through the control of the

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glass transition temperature. In this paper, we will deal with the rheological behavior of pure and formulated (i.e. with tackifying resins added) copolymers based, the polymer base being a blend of triblock and diblock copolymers. We will show how our systematic approach allows replacing classical copolymer blends by newly designed molecules in order to improve the processing end-user properties of the HMPSAs based on copolymers.

First of all, we will present the characteristics of the samples studied (linear polystyrene samples and block copolymers) and describe the rheological experiments performed on these samples. Then, we will summarize the theoretical basis of the rheological models which are based on molecular dynamics concepts. Hence, we will compare the results of the models prediction with experimental results. Finally, through two selected examples, we will propose trends of molecular design in order to improve (i) polymer processing (formulation of homopolymers) and (ii) HMPSAs processing and end-user properties (molecular design of copolymers).

2. Experimental

2.1. Rheological experiments

The rheological characterization of all samples is based on measurements of the complex shear modulus (G' and G'') as a function of circular frequency ω , at various temperatures. These mechanical spectroscopy experiments have been performed in a large frequency range using Rheometrics RDA II, ARES or DSR rotational rheometers in parallel-plate geometry. At high temperature, the measurements have been performed under dry nitrogen atmosphere. The time–temperature superposition principle can be used to plot the data which exhibit the various relaxation domains ranging from the terminal zone (flow region or rubbery and secondary plateau regions for viscoelastic solids like [SIS] and blends) up to the glassy domain (T_α relaxation) at high frequencies. For the copolymers under study, which exhibit different microstructural organizations depending on temperature [8–10], one can notice that the maximum temperature to which the time–temperature superposition principle still applies is about 30 °C. For polystyrene samples, master curves have been built at 200 °C and for copolymers samples is 20 °C.

The diameters of the plates were varied from 5 to 25 mm depending on the modulus level, in order to minimize instrument compliance and sample slip effects, particularly in the glassy domain. We have calculated the linear stress growth at flow start-up from the complex modulus data. In order to compare with the transient elongational stress growth data performed on PS 1 and 2 and blends A and B. The uniaxial elongational flow measurements have been performed at 160 °C at a strain rate of 0.1 s⁻¹ on a Rheometrics RME elongational rheometer using a contra-rotative clamps technique. A video post-treatment is performed in order to access the true

Table 1
MWD parameters of the used pure PS and their blends

Sample	M_w (kg mol ⁻¹)	I_{p1}	I_{p2}	I_{p3}	ϕ_3 (%)
PS 1	295	2.17	1.56	1.37	–
PS 2	190	1.03	1.03	1.04	–
PS 3	1480	1.16	1.08	1.06	–
Blend A (PS 2 and 3)	240	1.2	2.2	2.8	3.16
Blend B (PS 2 and 3)	320	1.6	2.82	1.97	10

elongational rate. If a discrepancy larger than 10% is found between to repetitive experiments, these data are discarded and a new run is performed.

2.2. Samples

2.2.1. Origin of the samples

PS 1 is a commercial sample which was kindly provided by Dow Benelux B.V. (Terneuzen, Netherlands) in the framework of a European project (3PI: postpone processing instabilities). PS 2 and 3 are narrowly distributed samples from, respectively, PolySource and ATOFINA companies.

The HMPSA samples described in this paper are formulated from blends of specific monodisperse block copolymers based on styrene and isoprene. The full formulations are made of blends of [SIS] triblock and [SI] diblock copolymers with added tackifying resins (see Table 2 for details on pure copolymers). The copolymers were synthesized by the Dexco Company (Houston, TX, USA) [6,7]. In this work, we have used two tackifying resins (which are oligomers compatible with the isoprene sequences and non-compatible with the polystyrene sequences): a solid resin (its glass transition temperature T_g being +47 °C), Escorez[®] 1310 from ExxonMobil Chemical Company (Houston) and a liquid resin ($T_g = -28$ °C), Wingtack[®] 10 from the Goodyear Company (Akron, OH, USA). The resins, which are added with a fixed concentration with respect to the copolymers, have a double effect on the isoprene elastomeric sequence of these structurally well-defined copolymers: a thermodynamical effect on the glass transition T_g and a topological effect on the plateau modulus which have already been extensively described in previous papers [11,12].

A series of blends have been made with different physical and structural parameters (see Table 3). In this paper, we will focus on the different ratios of diblock copolymer in the blend. The other parameters are roughly constant and then affect slightly rheological properties of the blends [6].

We introduce the three first indexes of polydispersity: $I_{p1} = M_w/M_n$, $I_{p2} = M_z/M_w$ and $I_{p3} = M_{z+1}/M_z$. We have reported the molecular parameters of the pure polymers, copolymers and blends in Tables 1–3.

Table 2
Characteristic parameters of pure copolymers

Pure copolymers	M_w (g mol ⁻¹)	S (%)
SI	72000	15
SIS	118000	18.2

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