

Feature Article

Evaluation of different methods for the determination of the plateau modulus and the entanglement molecular weight

Chenyang Liu^{a,b}, Jiasong He^b, Evelyne van Ruymbeke^{a,1},
Roland Keunings^{c,*}, Christian Bailly^{a,*}

^a *Unité de Chimie et de Physique des Hauts Polymères, Université catholique de Louvain, B-1348 Louvain-La-Neuve, Belgium*

^b *Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China*

^c *CESAME, Université catholique de Louvain, B-1348 Louvain-La-Neuve, Belgium*

Received 15 March 2006; received in revised form 26 April 2006; accepted 26 April 2006

Abstract

We critically evaluate and compare all major published methods for the experimental determination of the plateau modulus for monodisperse as well as polydisperse polymers with linear architecture. For long-chain monodisperse model systems ($M_w/M_n < 1.1$ and number of entanglements > 20 – 30), the various methods show excellent agreement, within an error margin of 5–10% close to the experimental uncertainty. For low numbers of entanglements, the terminal peak integration method requires a careful extrapolation at the high frequency side. This is best achieved by a simple subtraction of the Rouse relaxation. The universal terminal relaxation concept is validated for long chains, in logical agreement with tube model concepts. We further analyze the extension to polydisperse polymers of the methods validated for monodisperse systems. Agreement between the methods within a 15% range can be achieved in favorable cases. The preferred method is the terminal peak integration, with the same caveats as for monodisperse samples. Predictions from tube models can nicely complement other approaches but should be used with caution because they are sensitive to errors on the experimentally determined molecular weight and distribution. Methods based on the ‘crossover’ modulus are only semi-quantitative. A cross-check of all available methods is the best way to achieve maximal accuracy for polydisperse systems.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Plateau modulus; Viscoelastic properties; Tube models

1. Introduction

Since, the seminal work of de Gennes [1] and Doi and Edwards [2], tube theories have made spectacular progress and have, in a sense, become the ‘standard model’ of polymer physics. Because they cleverly simplify the hugely complex topological interactions between real macromolecules into a mesoscale mean field description, tube models show a unique balance of ‘economy’, sound physical basis and relative tractability. Their success is demonstrated by the quality of predictions made for the linear as well as non-linear

viscoelastic properties from knowledge of molecular weight distribution and architecture [3–7]. Tube models have also enabled the development of increasingly robust schemes for solving the so-called inverse problem for linear polymers, i.e. inferring the molecular distribution from the rheological response [8–16]. In all tube models, the fundamental parameter describing the topological network is the molecular weight between entanglements M_e . Hence, tube models should only require two adjustable scaling parameters, one for the time scale and one for the stress scale, both linked to M_e . The basic time scaling parameter is usually taken as τ_e , the equilibration time of a segment between entanglements. The basic stress scaling parameter is the plateau modulus G_N^0 . The tube picture provides an unambiguous relationship between M_e and G_N^0 , provided that consistent definitions are used. This has recently been clarified in a definitive review by Larson et al. [4]. Unfortunately, while model inconsistencies can lead to typical errors of 20% for G_N^0 , experimental values (noted $G_{N, \text{exp}}^0$ in the remainder of the manuscript) sometimes show a much larger

* Corresponding authors. Tel.: +32 10 478412; fax: +32 10 451593.

E-mail addresses: roland.keunings@inma.ucl.ac.be (R. Keunings), christian.bailly@uclouvain.be (C. Bailly).

¹ Present address: Foundation for Research and Technology-Hellas (FORTH) P.O. Box 1527, 71110 Heraklion, Crete, Greece.

spread. For example, $G_{N \text{ exp}}^0$ values ranging from 1.1 up to 2.6 MPa have been reported for polyethylene (PE) [17–26], and for bisphenol-A polycarbonate (PC), figures range from 1.2 up to 4.1 MPa [21,27–31]. The latter example is particularly revealing because no differences in molecular microstructure can be invoked to explain the situation. Clearly, the experimental evaluation of $G_{N \text{ exp}}^0$ is in many cases the limiting factor for an accurate description of the entanglement network rather than subtle differences between models. Various methods for $G_{N \text{ exp}}^0$ determination have been published over the years [17] and it has become increasingly important to systematically test, compare and possibly improve their accuracy as well as consistency.

The purpose of this work is twofold. First, for polymers with low polydispersity, our main goal is to check the consistency between published methods. Indeed, precise measurements on narrow disperse polymers are essential for testing the predictions of tube models in general. Residual discrepancies between definitive experimental data and theoretical predictions should help highlight shortcomings of the models. An important example of such a concern is the effect of finite chain-length on $G_{N \text{ exp}}^0$. Significantly different predictions have been published by Kavassalis and Noolandi [32–34], Likhtman et al. [3] and Masubuchi et al. [35]. Those predictions should be confronted with unquestionable experimental data. Another important example concerns universal methods for relating polymer structure to macroscopic properties, including M_e and G_N^0 [36,37]. Fetters et al. has suggested that viscoelastic properties can be correlated with chain dimensions, in particular the packing length [21,38–40]. Again, definitive $G_{N \text{ exp}}^0$ data are a prerequisite to test such approaches.

Our second objective is concerned with polydisperse polymers. As opposed to model systems, industrial polymers usually have broad polydispersity. Some systems (step condensation polymers for instance) cannot even be synthesized with polydispersity smaller than two. We, therefore, want to investigate the possible extension of methods for $G_{N \text{ exp}}^0$ determination to polymer systems with broad distribution, in particular systems with polydispersity around two.

This paper is divided into six sections. In Section 2, we review the definition of entanglement spacing and discuss published methods for determining the plateau modulus of monodisperse polymers, as well as the assumptions and modifications necessary to adapt these methods to polydisperse systems. In Section 3, we describe the polymers used in this study, and include published experimental data as well as predictions from recent tube models. In Section 4, we assess the consistency and applicability of published methods by analyzing the dynamic moduli of monodisperse model polymers. We also briefly compare the observed molecular weight (MW) dependence of $G_{N \text{ exp}}^0$ with theoretical predictions. In Section 5, modified methods for polydisperse polymers are analyzed and compared. Applications of the methods are illustrated by two important examples. Conclusions are presented in Section 6.

2. Theory and published methods

2.1. Definition of entanglement spacing and time

In tube models, the entanglement molecular weight M_e , defined as the average molecular weight between topological constraints, is the most fundamental material parameter, as envisioned by Edwards and de Gennes. M_e cannot be easily measured in a direct fashion and is usually inferred from the plateau modulus G_N^0 , which can be determined by measuring the dynamic moduli G' and G'' in oscillatory shear experiments:

$$G_N^0 = \frac{4}{5} \frac{\rho RT}{M_e}. \quad (1)$$

We follow the ‘G definition’ of the entanglement spacing [4], which means that the ‘number of entanglements’ per molecule, $Z = M/M_e$, is equal to the number of tube segments per molecule. On the other hand, M_e (or equivalently, the tube diameter a) also can be extracted from other experimental techniques [6], but those methods are restricted to a few polymer species [41], and the results need to be cross-checked with other techniques [42,43]. In present study, only the determination of G_N^0 by rheological methods is discussed.

Fig. 1 shows the master curve of the storage and loss moduli for a linear polybutadiene (PBD) with narrow molecular weight distribution (MWD) and very high MW (obtained from [44]). The characteristic times of different relaxation modes correlate with M_e via the number of entanglements Z as follows

$$\tau_R = Z^2 \tau_e, \quad (2)$$

$$\tau_d = 3Z^3 \tau_e, \quad (3)$$

where τ_R is the Rouse relaxation time of the chain, τ_e is the relaxation time of a segment between entanglements, and τ_d is the reptation disengagement time, uncorrected for contour length fluctuations (CLF).

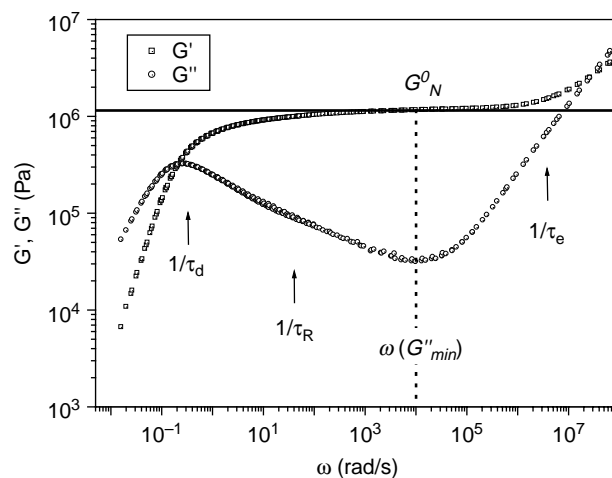


Fig. 1. Master curve of the storage and loss moduli for a monodisperse long chain polymer. Data for polybutadiene with $M_w = 410$ kg/mol and $Z \sim 260$ were obtained from Wang et al. [44].

Download English Version:

<https://daneshyari.com/en/article/5189482>

Download Persian Version:

<https://daneshyari.com/article/5189482>

[Daneshyari.com](https://daneshyari.com)