Characterisation of an Industrial Polymer Melt Through either Uniaxial Extension or Exponential Shear Data: An Application of the Pom-Pom Model

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Abstract:
We present new non-linear data in extension and two different shear histories. These data are used to compare the effectiveness of using exponential shear data and uniaxial extension data to characterise the non-linear response of an industrial LDPE melt with the pom-pom molecular model. We conclude that extension and exponential shear both allow good predictions to be made in simple shear. However, the characterisation spectrum obtained from exponential shear data fails to predict the correct degree of strain hardening at low extension rates. From this study we are able to suggest circumstances under which exponential shear provides a useful characterisation of branched polymer melts.

Zusammenfassung:
Wir präsentieren neue nicht-lineare Datensätze für Dehnverformung und zwei unterschiedliche Scherverformungen. Diese Daten werden benutzt, um die Güte rheologischer Daten in exponentieller Scherverformung und uniaxialer Dehnverformung von handelsüblichen LDPE Schmelzen mit dem Pom-Pom Modell zu vergleichen. Wir kommen zu dem Ergebnis, dass Dehnung und exponentielle Scherverformung gute Vorhersagen in einfacher Scherverformung erlauben. Das rheologische Spektrum, welches aus den exponentiellen Scherverformungsdaten gewonnen wird, versagt jedoch bei der Vorhersage der Dehnverfestigung bei kleinen Dehnraten. Auf Grund unserer Untersuchungen können wir Bedingungen angeben, für die exponentielle Scherverformung eine nützliche Charakterisierung verzweigter Polymerschmelzen darstellt.

Résumé:
Nous présentons de nouvelles données non linéaires en extension avec deux histoires de cisaillement différentes. Ces données sont utilisées afin de comparer l'efficacité des données de cisaillement exponentiels et des données d'extension uniaxiale afin de caractériser la réponse non linéaire d'un LDPE industriel à l'aide du modèle moléculaire type POM-POM. Nous concluons que l'extension et le cisaillement exponentiel permettent tous deux d'établir de bonnes prédictions pour le cisaillement simple. Toutefois, le spectre caractéristique obtenu à partir des données de cisaillement exponentiel ne parvient pas à prédir le degré correct de durcissement à la déformation pour les petites vitesses d'extension. Grace à cette étude, nous sommes en mesure de suggérer des conditions pour lesquelles le cisaillement exponentiel fournit une caractérisation efficace des fondus de polymères branchés.

Key Words: constitutive equations, pom-pom model, uniaxial extension, exponential shear, branched polymer

1 INTRODUCTION

Flows that are capable of producing large amounts of chain stretch in polymer fluids are ubiquitous in melt processing and are also important from both an experimental and theoretical point of view. They provide a challenging test for any theory in the non-linear regime. In addition, such stretching flows that test "melt strength" are sensitive to molecular detail which is essential when characterising a material from its non-linear response. Conversely, a practical measure characterising the extensional behaviour of a melt is needed by producers and processors alike. It is hoped that non-linear rheology will eventually become a sensitive probe of molecular structure and weight distribution. For an example of work in this area see Wood-Adams [1]. Many molecularly based constitutive equations model polymer molecules as Hookean springs. If embedded points in the flow separate exponentially as a function of time then this is sufficient

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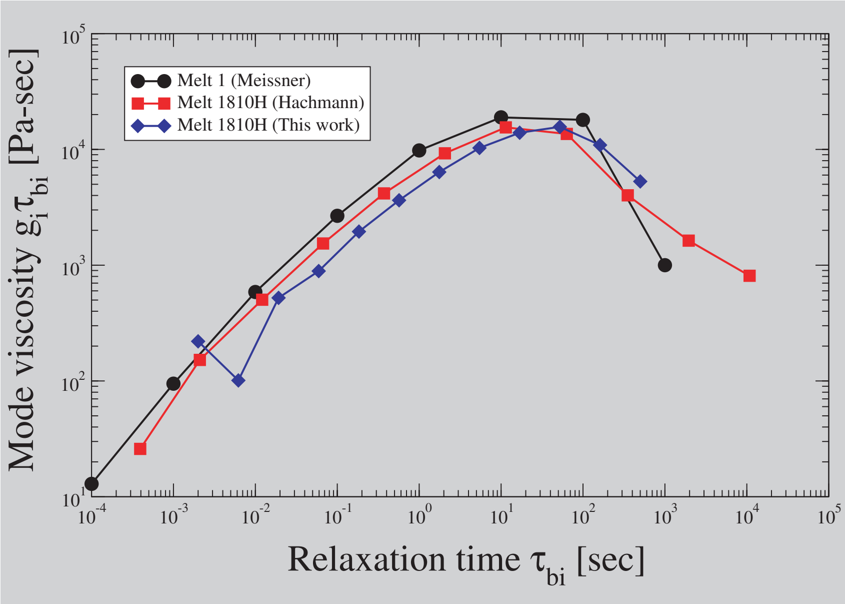

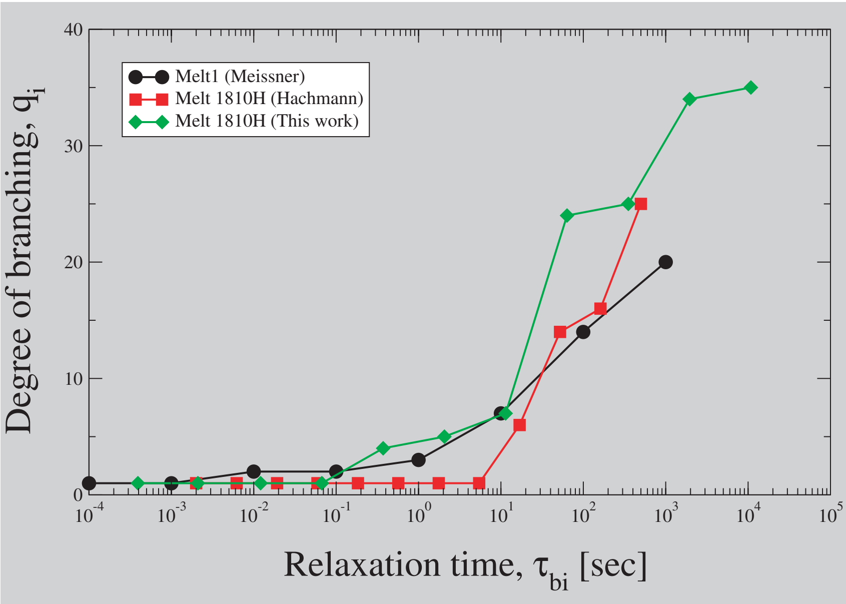

Figure 6 (above): Comparison of linear viscosity contribution, $g_i\tau_i$, against relaxation time, τ_i, for three similar LDPE melts.

Figure 7 (below): Plot of the spectrum of degree of branching, q_i, for three LDPE melts as obtained by pom-pom fitting to extensional rheology.

against mode relaxation time. For each melt the spectrum obtained from extensional rheology is shown since this is the most complete. This plot reveals the superiority of non-linear rheology over linear oscillatory shear in probing molecular detail. Both batches of melt 1810H have noticeably enhanced degrees of branching relative to melt 1 despite having almost identical linear behaviour. The pom-pom fitting also exposes variations in degree of branching between the two melt 1810H batches.

Earlier constitutive equations have had some success in fitting non-linear melt rheology using a multimode approach (for example see Bird et al. [16] for a comparison between LDPE melt rheology and an eight mode Giesekus model) but, for these models, the link between fitting parameters and molecular structure is unclear. Figure 7 demonstrates the ability of the pom-pom model to relate rheological data to molecular structure. It should be noted that, due to the intra-molecular decoupling approximation of the multimode pom-pom model, these values do not represent absolute degrees of branching. However, the physics of the pom-pom model makes clear the link between branching structure and rheological response and this connection is retained in the multimode pom-pom model. For a detailed discussion of the link between molecular branching and multimode pom-pom parameters see Blackwell [17].

6 CONCLUSIONS

We have independently fitted the exponential shear and extensional data and shown that spectra obtained from either approach will capture the behaviour of strongly non-linear, shear dominated flows and rapid extensional flows, thus confirming experimentally the suggestion of Graham et al. [7]. Fitting to the extensional data can predict the slow modes better than the exponential shear as suggested by Graham et al. [7]. However these slow modes make a significant contribution to mechanical stresses only under very specific flow conditions, namely at large strains under slow extension. Many complex geometries will not probe this region of the model's constitutive behaviour and in this case a spectrum obtained only from exponential shear data will be sufficient to model such a flow. For examples of such computation with differential constitutive equations in complex geometries see Peters et al. [18] and Lee et al. [12]. We also conclude that normal stress measurements in shear provide insufficient characterisation information above that obtainable from shear stress data to justify the considerable experimental effort required to obtain these data. Finally, we have demonstrated the usefulness of the pom-pom model, in combination with non-linear rheological data, to obtain information about molecular structure that is not available from linear rheology alone.

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