

MACROSCOPIC MODELING OF A SINGLE ENTANGLEMENT AT HIGH DEFORMATION RATES OF POLYMER MELTS

A.YA. MALKIN*, A.V. SEMAKOV, V.G. KULICHIKHIN

Laboratory of Polymer Rheology, Institute of Petrochemical Synthesis,
Russian Academy of Sciences, 29 Leninskii prospect, Moscow 119991, Russian Federation

*Corresponding author: alex_malkin@mig.phys.msu.ru

Received: 27.2.2012, Final version: 23.4.2012

ABSTRACT:

We constructed a macroscopic model illustrating behavior of a single entanglement knot of macromolecules in a melt and examined its behavior at different deformation rates. A model consists of flexible elastic strips, which are tied in a granny knot (modeling not a real geometrical form of entanglements but their behavior at relatively easy sliding). This scheme models the situation when elastic energy exceeds the energy of the Brownian motion. The behavior of a knot chosen for modeling is different at low and high deformation rates. In the previous case knots disentangle as predicted by the "tube" model, elastic strips slip out a knot and this is an illustration of flow. In the latter case, knots tighten up, further extension of strips leads to the increase in stresses up to breakup of a strip. This effect imitates the transition from the flow to the rubbery-like behavior of polymer melts, when flow becomes impossible due to the formation of quasi-permanent entanglements. The general dimensionless correlation for the process under discussion has been proposed.

ZUSAMMENFASSUNG:

Wir erstellten ein makroskopisches Modell, das das Verhalten eines einzelnen Verschlaufungsknotens von Makromolekülen in der Schmelze beschreibt und untersuchten sein Verhalten bei unterschiedlichen Deformationsraten. Das Modell besteht aus flexiblen elastischen Streifen, die in einem sogenannten Altweiberknoten verbunden sind (nicht um eine reale geometrische Gestalt von Verschlaufungen, sondern um ihr Verhalten bei relativ geringem Gleiten zu modellieren). Dieses Schema modelliert die Situation, in der die elastische Energie größer als die Energie der Brownschen Bewegung ist. Das Verhalten eines Knotens unterscheidet sich bei niedrigen und bei hohen Deformationsraten. Im ersten Fall entschleuft sich der Knoten entsprechend dem Röhrenmodell. Die elastischen Streifen gleiten aus dem Knoten, was ein Beispiel für Fließen darstellt. Im dem zweiten Fall ziehen sich die Knoten fest. Eine weitere Dehnung der Streifen führt zu einer Verhöhung der Spannung bis zum Aufbrechen der Streifen. Dieser Effekt stellt den Übergang vom Fließen zum gummiähnlichen Verhalten von Polymerschmelzen dar, bei dem kein Fließen aufgrund der Bildung quasi-permanenter Verschlaufungen eintritt. Eine allgemeine dimensionslose Korrelation für diesen Prozess wird vorgestellt.

RÉSUMÉ:

Nous avons construit un modèle macroscopique illustrant le comportement d'un unique nœud d'enchevêtrement de macromolécules dans un fondu, et avons examiné son comportement à diverses vitesses de déformation. Le modèle consiste en des bandes élastiques flexibles qui sont nouées dans un nœud de vache (modélisant non une forme géométrique réelle pour les enchevêtrements, mais leur comportement pour un glissement relativement aisé). Ce schéma modélise la situation où l'énergie élastique excède l'énergie du mouvement Brownien. Le comportement du nœud choisi pour le modèle est différent pour des vitesses de déformation petites ou grandes. Dans le premier cas, les nœuds se déenchevêtrent ainsi que le prédit le modèle du tube, les bandes élastiques glissent en dehors du nœud et ceci est une illustration de l'écoulement. Dans le second cas, les nœuds sont liés, et une extension supplémentaire des bandes conduit à une augmentation des contraintes jusqu'à la rupture de la bande. Cet effet imite la transition depuis l'écoulement jusqu'au comportement de plateau élastique des polymères fondus, lorsque l'écoulement devient impossible à cause de la formation d'enchevêtrements quasi permanents. La corrélation générale adimensionnelle pour le processus discuté ici a été proposée.

Key Words: polymer melt, entanglements, elasticity, modeling, dimensionless criterion of breakup

The $G_{term} = J_{term}^{-1}$ value for polyisoprenes is $1.6 \cdot 10^5$ Pa, i.e. much higher than for polybutadiens and $\tau_s = 1.7 \cdot 10^5$ Pa [12], i.e. this value is lower than τ_s for polybutadienes. Direct measurements of the ratio (τ_s/G_e) for a set of samples with different molecular weights gave the value (τ_s/G_e) ≈ 0.45 [4] and consequently $G_e = 3.8 \cdot 10^5$ Pa. The value of the plateau modulus G_e for polyisoprene given in [10] equals to $4.7 \cdot 10^5$ Pa, but only for one sample. However, the difference is not critical. Then Equation 10 gives $M^* \approx 0.24$. The difference between polyisoprenes and polybutadiens is evident and is primarily related to the great difference in the elastic compliance of the two melts in the terminal zone.

However we suppose that the above discussed calculations should be treated mainly as some rough estimation, because the M_e values were determined in the linear region. Meanwhile, macro-modeling demonstrated that the deep rearrangements in the network structure occur in the transition from the linear to strong non-linear behavior [1]. Then due to the thickening of knots, a chain must go much longer path to slip out all entanglements, that can be treated as the increase in the apparent M_e . Indeed, treating a bundle (which appeared as the result of high deformations) to be a molecular unit, we would relate the Brownian movement to much larger volume than a single chain length between neighboring entanglements. At the moment, it is rather difficult to estimate the volume of this bundle but, surely, it includes at least several entanglement knots. So, one can expect that the liable disentanglement would require much more acts of the Brownian motion and consequently much higher M^* values should be expected.

The relationship between elastic energy and energy of Brownian motion (the M -criterion) can be different depending on the nature of a polymer. However, it is reasonable to think that at least in some cases the Brownian motion can be neglected and to suppose that elasticity is the dominating factor in the strong nonlinear region corresponding to the liquid-to-solid dynamic transition. This result means that the model of reptations should be treated with certain caution and chain disentanglements are unlikely possible at high deformation rates. The general result of this study is the experimental proof that macromolecular chains in a polymer melt do not

obligatory slip out from entanglements leading to disentangling (the mechanism of flow) but at high deformation rates, macromolecules can tighten up creating a quasi-permanent (in the experimental time scale) network. As a result, a melt becomes equivalent to a rubber with temporary bonds by its deformation behavior mode. It excludes a possibility to flow and as a final result, a sample breaks in the elastic-like manner at high enough deformation rates.

4 SUMMARY

A macro-model of knots formed by elastic strips allows us to observe the main peculiarities of deformations of entangled polymer chains: disentanglement and sliding (as a model of flow) at low speeds and tightening and breakup at high speeds (as a model of flow-to-rubbery transition). Knots are a mechanical analogue (but not geometrical scaling) of macromolecule interactions. The dimensionless analysis of deformation of elastic strips and their behavior in knots gives us the quantitative picture of this process and the threshold value corresponding to the flow-to-rubbery transition. The proposed macro-model is the illustration of the real behavior of polymer melts at different deformation rates.

ACKNOWLEDGMENT

The work was supported by the Russian Foundation for Basic Research, Grant 10-03-00079a, and by Grant of the Section for Chemistry and Material Science of RAS for 2012. This work was partly presented at AERC-2011, Russia, Suzdal', May 2011.

REFERENCES

- [1] Malkin AYa, Semakov AV, Kulichikhin VG: Modeling Macromolecular Movement in Polymer Melts and its Relation to Non-linear Rheology, *Rheol. Acta* 50 (2011) 485-489.
- [2] Doi M, Edwards SF: *The Theory of Polymer Dynamics*, Oxford University Clarendon Press, New York (1986).
- [3] McLeish T: Molecular polymeric matter, Weissenberg, Astbury and the pleasure of being wrong, *Rheol. Acta* 47 (2008) 479-489.
- [4] Vinogradov GV, Malkin AYa, Yanovski YuG, Borisenkova EK, Yarlykov BV, Berezhnaya GV: Viscoelastic properties and flow of narrow distribution polybutadiens and polyisoprenes, *J. Polymer Sci. Part A-2* 10 (1972) 1061-1084.

- [5] Malkin AYa, Petrie CJS: Some conditions for rupture of polymer liquids in extension, *J. Rheol.* 41 (1997) 1-25.
- [6] Filip P, Svrčinova P Measurement of elongational viscosity of polymer melts using SER Universal Testing Platform, *Appl. Rheol.* 22 (2012) 14776.
- [7] Malkin AYa, Semakov AV, Kulichikhin VG: Non-Newtonian flow of polydisperse polymer melts as a consequence of the changes in their relaxation spectrum, *Polym. Sci.* 54 (2012) to be published.
- [8] Malkin AYa, Leonov AI: Unstable flow of polymers, in *Advances in polymer rheology*, G.V. Vinogradov (Ed.), Khimiya Publ., Moscow (1968) 109.
- [9] Vinogradov GV, Malkin AYa, Volosevitch VV, Shatalov VP, Yudin VP: Flow, high-elastic (recoverable) deformations and rupture of uncured high MW linear polymers in uniaxial extension, *J. Polymer Sci.: Polymer Phys. Ed.* 13 (1975) 1721-1735.
- [10] Auhl D, Ramirez J, Likhtman AE, Chambon P, Ferrybough Ch: Linear and nonlinear shear flow behavior of monodisperse polyisoprene melts with a large range of molecular weights, *J. Rheol.* 52 (2008) 801-836.
- [11] Rasmussen HK, Bejenariu AG, Hassager O, Auhl D: Experimental evaluation of the pure configurational stress assumption in the flow dynamics of entangled polymer melts, *J. Rheol.* 54 (2010) 1325-1336.
- [12] Vinogradov GV, Malkin AYa: *Rheology of polymers*, Springer, Heidelberg, Berlin (1980).

