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Molecular dynamics studies of entangled polymer chains

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2008

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Bulacu, M. I. (2008). *Molecular dynamics studies of entangled polymer chains*. s.n.

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Chapter 7

Concluding remarks

One must stop before one has finished.

Barbara Tuchman

This chapter summarized the overall results of this study and connect them with the goals of the thesis. The crucial importance of including chain stiffness in the chain model used for molecular dynamics simulations of dense entangle polymer chain ensemble is highlighted. The thesis is concluded by a short outlook of the possible future research directions that can be followed for a more in-depth study of polymeric materials.

7.1 Summary and contributions

This thesis is mainly devoted to the study of the dynamics of dense polymer chain ensembles in the melt or glassy state, and during a very common application: polymer-polymer adhesion reinforced with connector chains. Since polymer dynamics is a very complicated multi-body problem that cannot be solved analytically, a powerful alternative is to use molecular dynamics simulations. Nevertheless a reasonable polymeric system contains an enormous number of chains that interact with each other, and the simulation of such system becomes a very difficult task. Luckily the last decade brought an enormous computer development that has enabled the work presented here.

The motion of an individual chain from such *fascinating systems of mobile entangled chains*¹ is characterized by the diffusion coefficient, the analysis of Rouse modes, the autocorrelation functions, or by its direct effects on the adhesion strength.

The results presented in the thesis are compared with the two most famous theories about chain motion:

(1) *Rouse theory* which predicts that the chain center of mass moves like a Brownian particle if the chain is small enough not to entangle with the other chains (Rouse 1953);

(2) *reptation theory* which states that the motion of a long entangled chain is confined inside a "tube" formed by the constraints imposed by the entanglements with the other chains (de Gennes 1979, Doi and Edwards 1989).

The chain length at which these models overtake dominance is known as the entanglement length N_e . At the moment of writing of this thesis there is a big debate in the theoretical and modeling community about how this length is affected by the chain stiffness.

The motion of the chains inside a dense polymeric ensemble of entangled chains is ultimately revealed in the macroscopic properties of the material (e.g. the glass transition or the adhesion strength). So there is a great interest in understanding the chain dynamics when trying to control such properties for technical applications. One question rising from an adhesion application is if stiffer connectors are better adhesion promoters than flexible connectors. This was the initial motivation to extensively explore the chain stiffness as a variable parameter in the polymer dynamics, first in polymer melts and glasses, and then in adhesion setups. The fundamental inquiry that appears is if stiffness manifests itself as a universal phenomenon with scaling properties or will have some peculiar properties.

Because of the long length and time scales associated with polymeric materials, a coarse grained bead-spring model has been used to represent the polymer chains, following the model proposed by Kremer and Grest (1990). Each chain is treated as a

¹P.-G. de Gennes in the preface of *Scaling Concepts in Polymer Physics*

linear sequence of beads interconnected by springs, every bead representing a group of a few atoms or monomer units along the polymer backbone. All the pair beads in the system interact via a repulsive Lennard-Jones potential while the consecutive connected beads feel an extra anharmonic potential to maintain the chain connectivity. The dynamics of a polymer melt is determined by the entanglement between the chains of the ensemble, and this has direct implications on the physical properties of the system, including phase transitions and T_g . Such model already leads to an intrinsic stiffness of the polymer chains due to the excluded volume interaction.

Supplementary, in the work presented here, the chain stiffness is enhanced by adding bending and torsion potentials along the chain. For this purpose, a novel torsion potential acting both on dihedral and bending angles is proposed following a tentative suggestion of Scott and Scheraga (1966) and Pauling (1960). In this way the torsion angles are controlled by an efficient continuous potential, rather than by using computationally expensive rigid constraints. The computational instabilities arising when two successive bonds align are naturally eliminated allowing long time simulations of large systems in order to perform diffusion studies.

In Chapter 4 the static and dynamic properties of a polymer melt have been investigated at a fixed temperature, for different chain lengths and stiffness. For intrinsic stiffness only (no bending, no torsion potentials) the results of Kremer and Grest (1990) are recovered showing a clear crossover from the Rouse regime to the reptation regime at the entanglement length. As the chain stiffness increases, the diffusion coefficients decrease for all chain lengths. The conventional Rouse regime, as defined from diffusion coefficient versus chain length, modifies progressively until it cannot be distinguished from the reptation regime. The specific length at the crossover between these two regimes (modified Rouse and reptation) shifts to larger polymer lengths until it becomes ill defined, indicating that the entanglement length increases with the chain stiffness. Further visualization of the motion of short polymer chains excludes the possibility of reptation for short stiff chains. The explanation for the Rouse regime modification may reside in the difference between glass transition temperatures of systems with different stiffness. As a consequence the systems may be more in the melt or in the glassy state at the fixed simulation temperature employed ($T = 1\varepsilon/k_B$).

This motivated the work presented in Chapter 5 in which the influence of chain stiffness is studied together with the influence of the temperature. In order to have better statistics (more polymer chains), this study is limited to short chains. The diffusion coefficient versus chain length dependences for stiff chains show the recovering of the Rouse regime as the temperature increases and no crossover to reptation in the length interval covered. This proves again that the entanglement length does not decrease with chain stiffness.

The diffusion results are also used to determine the glass transition temperature as

the limiting value where diffusion vanishes. The obtained values have been found also from the analysis of the relaxation times of the autocorrelation functions for the torsion angle and for the end-to-end distance proving the versatility of this model to capture the glass transition phenomenon (especially when chain stiffness is considered). As expected, stiffer chains lead to a higher glass transition temperature T_g .

Once it was demonstrated that the glass transition can be captured in molecular dynamics simulation using coarse-grained models for polymer chains, the adhesion fracture simulations of two glassy polymers reinforced with connector chains were possible. When the two polymers are separated the connector chains are pulled-out from the bulks until the adhesion is broken. The way the connectors are extracted from the polymers can be considered as a "forced/accelerated reptation": if the chains are short they move as a whole sustaining an overall deformation; if the chains are long and well entangled with the chains of the bulks, the deformation will propagate from the interface to the chain end. The chain length at which these two processes switch may be seen as an entanglement length for forced reptation and determine the fracture mechanisms (chain pullout). An extensive investigation of the connector chain architecture, rate dependence and temperature is included in Chapter 6. The dependences of the adhesion strength on connector length as n^2 , on areal density as Σ^1 , and on pulling velocity as v_{pull}^α (with α dependent on temperature) have been recovered for different number of stitches and for different stiffness along connectors. The time evolutions of the adhesion work from debonding simulations performed at various temperatures and pulling velocities collapse on a master curve when plotted in normalized units. An interesting observation concerns the number of stitches at the interface: the adhesion strength is not markedly influenced by increasing the numbers of stitches. For a given areal density of the connectors with the same length, the multi stitch configuration is only slightly stronger than the one-stitch configuration.

7.2 Further research directions

The results presented in this thesis prove the versatility and efficiency of coarse grained models for studying polymeric materials by molecular dynamics simulations. Both diffusion and adhesion studies presented in the thesis are able to reveal fundamental aspects specific for dense ensembles of polymer chains under the influence of chain stiffness: entanglement, glass transition, or adhesion properties.

By reaching the current development at the theoretical and modeling level multiple appealing research topics have inevitably shown their importance. These include small variations of the current model or autonomous investigation themes that were revealed during the study presented here, but have been disregarded for the moment in order to

keep the model as simple as possible.

On the other hand the investigation on polymer-polymer adhesion reinforced with connector chains detailed in Chapter 6 can be considered just the tip of the iceberg due to the very large palette of simulations that may continue. A few of the most important research directions are:

Extended studies involving the same model

1. An intriguing question that remains to be answered is: what is the polymer chain dynamics for long stiff chains at high temperatures? This thesis reported a recovering of the Rouse regime for short stiff chains when the temperature is raised well above the glass transition temperature; a crossover to the reptation regime is expected by increasing chain length, as for flexible chains. Such a finding together with the evaluation of the entanglement length N_e may be a proof of the scaling concepts in polymer dynamics: stiff chains can be considered flexible chains when the bead size is increased.
2. In many applications, fracture of polymer-polymer systems occurs as a result of shear loading or mixed tensile-shear loading. These possibilities of debonding are already included in the developed code but they have to be unified in a consistent study.
3. To adjust better to experimental conditions, the two polymer bulks and the connectors may be modeled as dissimilar polymers.

Modifications of the model

1. Considering a high areal density of connector chains at the interface allows for the observation of other specific fracture mechanisms (e.g. craze). For this, new techniques for generation and equilibration of the connectors prior to fracture have to be developed (the initial distribution is different from the case of low areal density covered in this study).
2. In the current stage of the code, the simulation stops when a connector is broken. An improved variant has to include the possibility of connector scission during debonding.
3. The polymer bulks may be modified by introducing chain crosslinks.

Autonomous research topics

1. In the current adhesion study the two polymer bulks to be bonded by the connectors have been considered completely non-interacting in order to clearly separate

the effect of the connector architecture. In this way an important aspect has been neglected: the interface. There is no doubt that the chemical and morphological structure of the interface region differs from that of the bulk (including the glass transition temperature) and, even the polymer bulks are immiscible, this region will affect the total adhesion strengthening. Therefore, an extended study dedicated to the polymer-polymer interface is imperative in future research.

2. Another open problem is the mechanical response of a single polymer bulk under deformation. This kind of study can be developed in two directions: (1) A comprehensive comparison between the present diffusion calculation and such future viscoelastic calculations especially for the effects of chain length and stiffness; (2) An improvement of the adhesion model by allowing both polymer bulks to deform during the fracture.
3. A possible computational challenge is to tune the coarse grained parameters to be specific for a real polymer. For this goal, detailed information from atomistic simulations of polymers is needed. However, the generic physics of the polymers is expected not to change essentially.