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Viscoelastic Properties of Polymer Systems From Dissipative Particle Dynamics Simulations

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14. ABSTRACT The U.S. Army has an increasing need for multifunctional polymers with specific viscoelastic properties. Such polymers are often present in nanocomposites, lubricants, or biomimetic gels that are used as tissue surrogate materials. Rational prediction of a polymer's viscoelastic properties necessitates the use of multiscale modeling since vastly different time and length scales have to be considered. In this study, we will apply the dissipative particle dynamics (DPD) method that is a fast and accurate alternative to traditional molecular simulations. The DPD method is a particle-based, coarse-grained mesoscale method. In this study, the simulation of viscoelastic properties is carried out by applying an additional, oscillatory shearing force. This oscillatory shear and corresponding stress allows us to calculate the storage (G') and loss modulus (G'') that define the viscoelastic behavior of polymer systems. As a demonstration exercise, the G' and G'' moduli were calculated for a diblock copolymer at low frequencies.					
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Contents

Acknowledgments	iv
1. Introduction	1
2. Dissipative Particle Dynamics	1
3. Viscoelastic Property Calculations	4
4. Conclusions	5
5. References	6
Distribution List	7

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1. Introduction

Materials for many applications relevant to U.S. Army needs, ranging from lubricants to nanocomposites, are often designed to attain required viscoelastic properties. Biomimetic gels as tissue-surrogate materials used in designing devices to protect Soldiers against blunt-force trauma, the permselective membranes for Soldiers' protective clothing, elastomeric adhesives for composites and armor design, and the design of hypergolic fuel gels to minimize catastrophic failures of fuel containers are just a few examples in which viscoelastic properties of materials are of critical importance. A challenge in designing these types of systems is in the large parameter space which needs to be explored. Many variables characterize such polymer systems, including molecular weights, compositions, segmental interactions, and more. As a result, it is difficult to anticipate the concomitant changes to material properties and morphology, with for example, temperature. Trial-and-error approaches which rely on laboratory measurements are costly and time consuming. Thus, computational material science has played an ever-increasing role in the design of polymeric materials (Andzelm et al., 2006; Lísal et al., 2006). The viscoelastic properties of polymer systems depend on morphologies and structures that span over length and time scales which are inaccessible by molecular modeling. Therefore, coarse-grained, particle-based mesoscale models that retain only the most essential features of the polymer system must be utilized.

In this report, we outline a computational protocol that invokes a particle-based mesoscale method, dissipative particle dynamics (DPD) (Hoogerbrugge and Koelman, 1992; Koelman and Hoogerbrugge, 1993), to simulate the viscoelastic properties of various polymer systems (Sen et al., 2005; Pryamitsyn and Ganesan, 2006). This tool will be invaluable to U.S. Army scientists in accelerating the design of materials with superior viscoelastic properties. In section 2, a brief overview of the dissipative particle dynamics method is given, followed by a description of the approach to calculate the viscoelastic properties using an oscillatory shear technique (Pryamitsyn and Ganesan, 2006) in section 3, followed by conclusions in section 4.

2. Dissipative Particle Dynamics

The DPD method is a mesoscale simulation technique that operates at time and length scales larger than those of traditional molecular dynamics, but for situations that are inaccessible to continuum dynamics (Hoogerbrugge and Koelman, 1992; Koelman and Hoogerbrugge, 1993). A DPD system is composed of soft particles, each representing a region of fluid, which moves continuously in space and discretely in time. In a DPD simulation, the polymer chain is modeled

as a collection of point particles that represent lumps of the chain containing several segments. DPD particles are defined by a mass m_i , r_i , and velocity v_i , and interact with each other via a pairwise, two-body, short-ranged force F that is written as the sum of a conservative force F^C , dissipative force F^D , and random force F^R :

$$\mathbf{F}_{ij} = \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R . \quad (1)$$

F^C includes a soft repulsion force F^{Cr} acting between two particles and a harmonic spring force F^{Cs} acting between adjacent particles in a polymer chain. Therefore, the DPD polymer chains are flexible since no additional constraints such as bond bending or bond torsion are included. F^{Cr} and F^{Cs} are given by

$$\mathbf{F}_{ij}^{Cr} = \begin{cases} a_{ij} \left(1 - \frac{r_{ij}}{r_c} \right) \frac{\mathbf{r}_{ij}}{r_{ij}} & \text{for } r_{ij} < r_c \\ 0 & \text{for } r_{ij} \geq r_c \end{cases} \quad (2)$$

and

$$\mathbf{F}_{ij}^{Cs} = -K \left(r_{ij} - r_0 \right) \frac{\mathbf{r}_{ij}}{r_{ij}}, \quad (3)$$

respectively. In equations 2 and 3, a_{ij} is the maximum repulsion between particle i and particle j , $r_{ij} = r_i - r_j$, $r_{ij} = |\mathbf{r}_{ij}|$, r_c is the cutoff radius, K is the spring constant, and r_0 is the equilibrium spring length. Conservative potential energies corresponding to F^{Cr} and F^{Cs} , u^{Cr} and u^{Cs} , can be expressed as

$$u^{Cr}(r_{ij}) = \begin{cases} \frac{a_{ij}}{2} \left(1 - \frac{r_{ij}}{r_c} \right)^2 r_c & \text{for } r_{ij} < r_c \\ 0 & \text{for } r_{ij} \geq r_c \end{cases} \quad (4)$$

and

$$u^{Cs}(r_{ij}) = \frac{K}{2} (r_{ij} - r_0)^2 . \quad (5)$$

The remaining two forces, F^D and F^R , are given by

$$\mathbf{F}_{ij}^D = -\gamma \omega^D \left(\mathbf{r}_{ij} \right) \left(\frac{\mathbf{r}_{ij}}{r_{ij}} \cdot \mathbf{v}_{ij} \right) \frac{\mathbf{r}_{ij}}{r_{ij}} \quad (6)$$

and

$$F_{ij}^R = \sigma \omega^R(r_{ij}) \frac{\xi_{ij}}{\sqrt{\Delta t}} \frac{r_{ij}}{r_{ij}}, \quad (7)$$

where $\omega^D(r)$ and $\omega^R(r)$ are weight functions that vanish for $r > r_c$, γ is the friction coefficient, σ is the noise amplitude, $v_{ij} = v_i - v_j$, ξ_{ij} is the Gaussian random number with zero mean and unit variance that is chosen independently for each pair of interacting particles, and Δt is the time step.

Español and Warren (1995) showed that the system samples the canonical ensemble and obeys the fluctuation-dissipation theorem (in the limit of $\Delta t \rightarrow 0$) if the following relations hold:

$$\omega^D(r) = [\omega^R(r)]^2, \quad (8)$$

and

$$\sigma^2 = 2\gamma k_B T, \quad (9)$$

where T is the temperature and k_B is Boltzmann's constant. $\omega^D(r)$ and $\omega^R(r)$ are typically chosen as

$$\omega^D(r) = [\omega^R(r)]^2 = \begin{cases} \left(1 - \frac{r}{r_c}\right)^2 & \text{for } r < r_c \\ 0 & \text{for } r \geq r_c \end{cases}. \quad (10)$$

The evolution of DPD particles in time t is governed by Newton's equations of motion:

$$\frac{dr_i}{dt} = v_i(t), \quad (11)$$

and

$$m_i \frac{dv_i}{dt} = f_i(t) = \sum_{i \neq j} (F_{ij}^C + F_{ij}^D + F_{ij}^R). \quad (12)$$

For a more detailed description, see the original papers (Hoogerbrugge and Koelman, 1992; Koelman and Hoogerbrugge, 1993).

3. Viscoelastic Property Calculations

The substantial effort underway to develop materials for U.S. Army applications with improved thermal and environmental stability and tunable viscoelastic properties require a broad range of strain rates (10^0 – 10^5 /s) and elastic moduli (0.1–2.6 MPa). Therefore, the theoretical methods which we propose must account for distinct physico-chemical processes occurring at vastly different strain rates. Both the measurements and calculations that attempt to characterize the dynamic mechanical properties use a relationship between the applied strain and the resulting stress in the material (Ferry, 1980). When the viscoelastic material is subjected to oscillatory strains, γ , of frequency ω , the stress response, σ , is necessarily cyclic and can be written as $\sigma(\omega) = G''(\omega) \gamma(\omega)$, where $G''(\omega) = G' + i\omega\eta$ and η is the viscosity. The storage modulus, G' , indicates the material's ability to store energy and the imaginary part of $G''(\omega)$, the loss modulus, $\omega\eta$, characterizes the amount of energy lost through the viscous process. Simulations can be used to determine which parameters govern the viscoelastic behavior of polymer systems, delineating the regimes and frequencies at which various effects (e.g., polymer chain length) are manifested.

The viscoelastic properties are calculated using a non-equilibrium oscillatory shear technique (Allen and Tildesley, 1987), which entails a simulation with an additional force in the shear direction along with time-dependent Lees-Edwards boundary conditions (Lees and Edwards, 1972). For oscillatory shear imposed in the xy -plane, the equation of motion for the particle velocities become

$$m_i \frac{dv_{ix}}{dt} = f_{ix} + m_i r_{iy} \frac{d^2 \gamma(t)}{dt^2} . \quad (13)$$

The oscillatory strain can be taken as $\gamma(t) = A_\omega [1 - \cos(\omega t)]$, where A_ω and ω are the chosen values of the amplitude and frequency, respectively. For the Lees-Edwards boundary conditions, the simulation box and its images centered at $(x,y) = (\pm L, 0), (\pm 2L, 0), \dots$ are taken to be stationary. Boxes in the layer above, $(x,y) = (0, L), (\pm L, L), (\pm 2L, L), \dots$ are moving at a speed πL in the positive x -direction, where π is the shear rate. Boxes in the layer below, $(x,y) = (0, -L), (\pm L, -L), (\pm 2L, -L), \dots$ move at a speed πL in the negative x -direction.

Following equilibration of the structure, a series of stress trajectories are generated by imposing the oscillatory shear conditions. A sample output for a diblock copolymer system is given in figure 1. Note that numerical errors tend to be higher at low frequencies requiring averaging over more stress trajectories to minimize these errors.

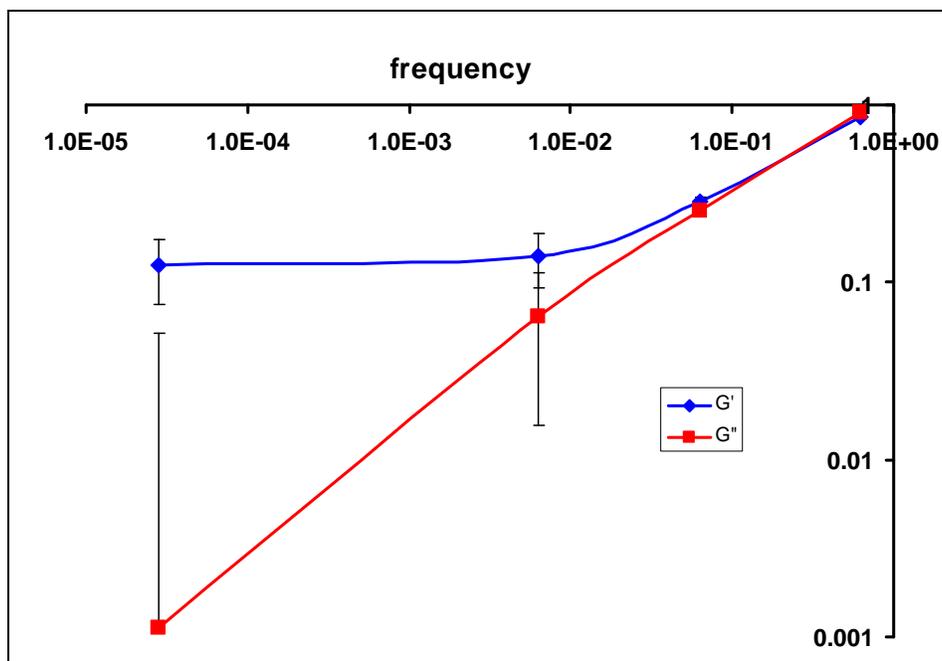


Figure 1. Sample output for a model diblock copolymer system which has microphase separated in spherical domains.

4. Conclusions

In this report, we have reviewed a computational method to calculate the viscoelastic properties of polymeric systems. We have used the DPD method and the non-equilibrium oscillatory shear technique as implemented in the code by Pryamitsyn and Ganesan to calculate the storage and loss moduli of the diblock copolymer. Such capability will be an invaluable tool for assisting material scientists in accelerating the design of materials with superior viscoelastic properties. Numerous U.S. Army applications such as multifunctional materials, coatings, hypergolic fuel gels, and elastomeric adhesives will greatly benefit from this tool.

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