

Effect of polymer solvent on the mechanical properties of entangled polymer gels: Coarse-grained molecular simulation

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ABSTRACT

Polymer gels are composed of a chemically or physically cross-linked polymer that is highly swollen with solvent. Two important limitations for the practical application of polymer gels are low toughness and a limited ability to tailor the strain-rate dependent mechanical response. Both these limitations are due to the high loadings of small molecule solvents that are typically incorporated into the gel formulation. Here, we provide insight into the role of physical entanglements on the performance of polymer gels, when the solvent molecular weight is large enough to entangle with the polymer network. Our simulations demonstrate that the solvent entanglements dominate the time-dependent elastic modulus of polymer gels with high-molecular-weight solvent. We have found that entanglement contribution to the modulus is essentially equal for the entangled polymer melt and loosely cross-linked entangled polymer gel at high strain rate. At lower strain rate, the modulus of the polymer gels develops a long-lived plateau that originates from “semi-trapped” entanglements formed between network strands and polymer solvent. The simulations were validated with selected experiments of chemically cross-linked polydimethylsiloxane (PDMS) elastomers loaded with a non-reactive silicone oil solvent, where the solvent molecular weight was varied. The simulations and experimental results demonstrate that highly entangled solvent can be used to tune the rate dependent modulus of polymer gels.

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1. Introduction

Polymer gels based on a physically or chemically cross-linked polymer network in the presence of solvent have utility in a broad range of military [1], industrial [2–4], and biomedical applications [5,6]. Mechanically, the solvent creates a “soft solid” that is easily deformable, yet still recovers from the deformation due to the elastic nature of the cross-links in the polymer [7]. Polymer gels offer potential in a wide array of applications because the gel properties can be tuned by varying the polymer chemistry [8], solvent type and processing conditions [9,1], solvent loading [10] and architecture of the polymer or solvent chains.

Polymer gels are extremely soft materials with a Young's modulus that typically ranges from 10^3 to 10^6 Pa, and this compliance is desirable for many applications such as electronic device encapsulation, and tissue engineering. The low stiffness of gels is due to the low cross-link density and high solvent loading present in the gel formulations. As a consequence of these formulations, two important factors limit the practical implementation of polymer gels including: low gel toughness, and a limited ability to tailor the strain-rate dependent modulus. Several efforts have been made to enhance the mechanical properties of polymer gels including strength, toughness and durability. These approaches have embraced usage of thermal cycling during processing [11,12], creating a double network [13,14] and synthesizing inorganic–organic hybrid materials [15]. However, far less research has focused on controlling the strain-rate dependence of the gel modulus.

While most gel formulations exploit small molecule solvents such as water or common polymer plasticizers, recent work has demonstrated that the rheological properties and toughness of the

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gel can be improved by utilizing polymeric solvents rather than small molecules [16]. In contrast with solvent composed of small molecules, when the polymeric solvent molecular weight is sufficiently large that it entangles with the polymer network and the frequency dependence of the modulus begins to increase when compared to the modulus of gels in non-entangled solvent [16]. The dynamic or relaxation modulus of these gels arises from the combined contribution of the cross-linked polymer network and the entangled solvent.

Viscoelastic properties of entangled polymers and networks are often described by the time-dependent stress relaxation modulus, $G(t)$. In Fig. 1 we sketch the stress relaxation modulus $G(t)$ against time on a log–log scale for two representative systems: a chemically cross-linked amorphous polymer and an amorphous polymer of high molecular weight. In the chemically cross-linked network, after a fast initial decay, the time-dependent relaxation modulus $G(t)$ stays nearly constant forming an equilibrium zone for a large range of time, $G(t) \approx G_c$, where G_c is the quantity treated by the theory of rubber like elasticity [17]. If the chains are long enough to have topological constraints or entanglements, $G(t)$ flattens at a somewhat higher value of the melt plateau modulus, G_N^0 , which is associated with the average monomer spacing between entanglements, N_e . At long times $G(t)$ of an uncross-linked polymer falls rapidly and eventually vanishes, which is associated with complete relaxation of the polymer chains. The plateau modulus for sufficiently long polymers ($N \gg N_e$) does not depend on their molecular weight, or number of monomers, N . At the same time, entanglements extend the time necessary to the long-range configurational changes and consequently polymers with higher molecular weight have $G(t) \approx G_N^0$ over a broader range of time or frequencies [17]. The contribution of chemical cross-links and entanglements to the stress of the entangled polymer networks are often assumed to be independent and additive [17,18]. In contrast, there are some models which postulate that the entanglement contribution to the shear modulus depends on the connectivity of the network [19–22].

The main objective of this paper is to understand the relative contributions to the mechanical and rheological properties of entangled polymer gels with polymer solvent by means of computer simulations. Here, we attempt to evaluate separately the contributions of cross-links and entanglements to the tensile stress and the relaxation modulus of the entangled polymer gels. The major obstacle in experimental study concerning the relationship between chain entanglements and the mechanical properties of polymers lies in the difficulty of isolating entanglement effects from the influence of other structural properties. Unlike an experiment, it is possible to decouple the entanglement effects in

computer simulations, which allows us to control and improve systematically the mechanical properties of the polymer gels, namely the elastic modulus.

Computer simulations have become a valuable tool for systematic evaluation of the mechanical properties of polymer systems. Direct atomistic modeling of dynamics of entangled polymers is still prohibitively time consuming [23–25] due to slow reptation dynamics exhibited by high-molecular-weight polymer chains, where center-of-mass diffusivity, \mathcal{D} , scales with polymer length as $\mathcal{D} \propto N^{-2.3}$ [26]. Coarse-graining models unites a large number of atoms into a coarse-grained particle and allows us to sample longer time scales and larger system sizes and thus coarse-grained models significantly reduce the necessary amount of CPU time. The dynamics of highly entangled polymer becomes even more computationally demanding and reptation models such as tube and slip-link models are applied for systematic evaluation of the mechanical properties of highly entangled polymer systems within acceptable computational cost. However, these theoretical descriptions have several adjustable parameters, which have not been related to microscopic details. These models become very complex for polymer gels due to the presence of two types of polymer chains: free entangled polymer chains and entangled network strands, subsequently some of the entanglements are permanent and the others can relax with time. There have been several theoretical and computational efforts undertaken to gain a physical understanding of characteristic features of the dynamics of the entangled polymer networks using a standard coarse-grained approach [27,28], and a slip-link model [22]. The first theoretical comprehensive study of stoichiometrically imbalanced polymer network (entangled network with dangling strands), has been recently presented by Jensen et al. [22] using a single-strand mean field discrete slip-link model (DSM). We are planning to employ DSM for the entangled polymer gels in our future studies.

Here, we use a standard polymer coarse-grained, bead-spring “Kremer–Grest” model [30,31] of a dense polymer system, which has proved to be an excellent technique to study microscopic topology and dynamics of a wide variety of entangled polymer systems [32–36]. In our study, we investigate the dependence of the mechanical properties of polymer gels on the molecular weight of solvent made of linear polymer chains. One of the goals of this study is to validate our computational approach to predict the mechanical properties of polymer networks with intricate architectures which are difficult to describe with semi-phenomenological theories. Computational results are compared with these theories and experimental deformation data on polydimethylsiloxane gels.

2. Model and methods

2.1. Polymer model

Polymer chains are represented by a coarse-grained bead-spring model with beads of mass m [31]. The pair interaction between topologically nonconnected (nonbonded) particles is described by the standard truncated Lennard-Jones pair potential

$$U_{LJ}(r) = 4U_0 \left[\left(\frac{a}{r} \right)^{12} - \left(\frac{a}{r} \right)^6 - \left(\frac{a}{r_c} \right)^{12} + \left(\frac{a}{r_c} \right)^6 \right], \quad (1)$$

where U_0 is the depth of the potential well and a is the separation distance at which the interparticle potential is zero, and r_c represents the cutoff distance. $r_c = 2^{1/6}a$ is chosen, yielding the so-called Weeks–Chandler–Andersen excluded volume potential, $U_{WCA}(r)$.

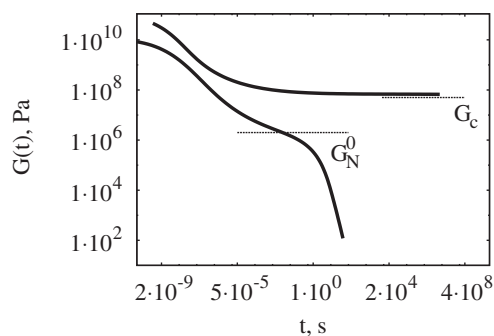


Fig. 1. Schematic representation of the stress relaxation modulus, $G(t)$. The upper and lower curves represent a cross-linked amorphous polymer and an amorphous polymer of high molecular weight without chemical cross-links, respectively.

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