

Elastic Stress and Strain Distributions in Polymeric Materials

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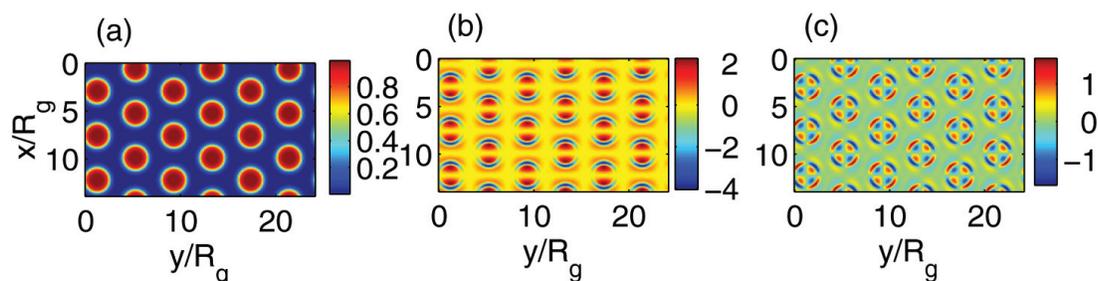
An understanding and modeling of the elastic properties of polymeric materials such as Estane®, which serves as the polymeric binder component in the high explosive PBX-9501, is an important issue for nuclear weapons. There are strong suggestions that aging effects in this composite arise from chemical and physical changes in the binder. Estane 5703 is a segmented block copolymer, the strength of which arises from the self-organization it undergoes.

Block copolymer melts in a microphase-separated state exhibit complex mechanical response and flow behavior that is fundamentally different from the behavior of chemically cross-linked materials such as rubber. Applied mechanical stress causes orientation phenomena, which in turn leads to the disruption and recombination of bonds into energetically favorable positions. These phenomena are thought to be responsible for the typical features of block copolymer materials such as high tensile strength, tear strength, and elongation. However, the interplay between self-assembly and elastic properties is sensitive to a wide range of variables, and a fundamental and comprehensive understanding has yet to be realized.

Our previously developed self-consistent field models can effectively and precisely determine the morphological structures emerging from the self-assembly of such segmented chains. In order to further enable this methodology to also characterize the elastic properties resulting from these self-assemblies, we have constructed a self-consistent field theory that in addition to the polymer density also incorporates the local stress and strain fields in the material. This development is based on previous work by Fredrickson [1] who recently developed a self-consistent field theory for homopolymer melts that simultaneously incorporates polymer density, stress, and strain fields. The strain is included at the microscopic level via a single chain expression due to Doi and Edwards [2]. The stress field arises as the conjugate to the strain field. We have extended this theory to self-assembling polymer systems, and we have initially computer-implemented this theory for the simplest such system, namely diblock copolymers.

Within this theory we are able to not only determine the morphological properties of the polymer density but also the corresponding internal stress distributions in the self-assembled structures. An example of this is

Fig. 1. Unstrained ($\epsilon = 0$) equilibrium phases and stress tensor components for 30:70 AB diblock copolymer. The corresponding tensor components σ_{xx} and σ_{xy} are also shown.



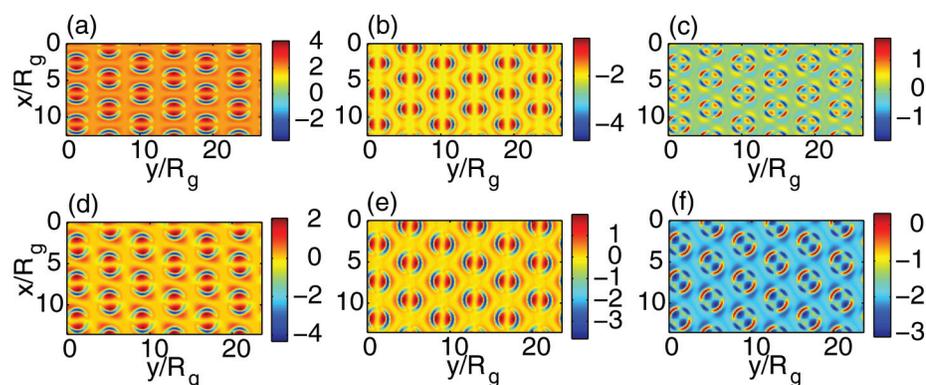


Fig. 2. Components of the stress tensor for two different nonzero strain applied to the hexagonal phase ($\text{tr } \epsilon = 0$ for both cases). For $\epsilon_{xx} = -0.1$, $\epsilon_{yy} = 0.1$, and $\epsilon_{ij} = 0$, for $i \neq j$ σ_{xx} (a), σ_{yy} (b), and σ_{xy} (c) are shown. For $\epsilon_{ij} = 0$, for all i, j except $\epsilon_{xy} = -0.1$ the components σ_{xx} (d), σ_{yy} (e), and σ_{xy} (f) are shown.

shown in Fig. 1 for the hexagonal phase of a diblock copolymer. In this particular case a block copolymer composed of just two different chemical species (say A and B) in the volume ratio 30:70 self-assembles into cylinders rich in the minority species (A), which are packed hexagonally in a matrix formed by the majority species (B). Together with a two-dimensional projection of polymer density we show a similar projection of the σ_{xx} and the σ_{xy} components of the stress tensor. Similarly, we can determine the remaining components of the stress tensor. Such stress distributions can also be determined in the presence of strain loadings (see Fig. 2), and closer scrutiny provides detailed understanding of the variation of stress along statistically typical polymer chains depending on their position in the overall structure of the self-assembled melt.

Our model further allows us to follow the behavior of the polymer melt in the presence of applied stress in greater detail as illustrated by Fig. 3 where we show the spatially averaged stress as a function of the external strain for the hexagonal phase. As expected it can be seen that a compression (expansion) of the melt, in the (i, j) directions, leads to

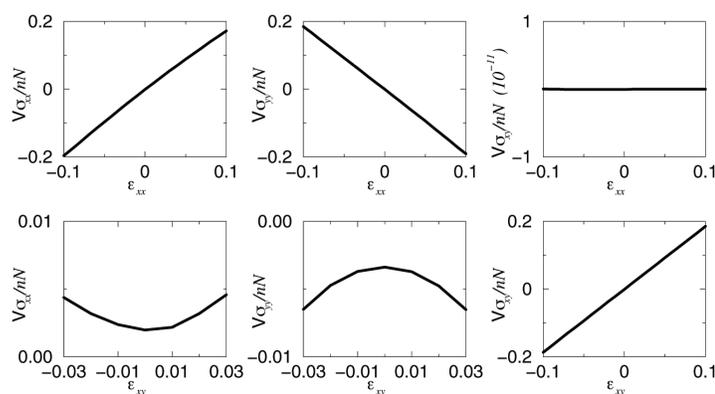


Fig. 3. The spatially averaged components of the stress tensor σ as a function of the external strain in the hexagonal phase.

a decrease (increase) of the spatially averaged stress in this direction (i.e. a change of σ_{ij}). As the applied strain undergoes the relatively large variation from -0.1 to 0.1 we see that the primary stress component changes linearly, while the more secondary elements display a nonlinear dependence for larger ($|\epsilon_{ij}| > 0.01$) applied strain. From the slope of the lines shown in Fig. 3 in the small strain region, it is possible to calculate the corresponding components of the elasticity tensor $K_{ij,kl}$.

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- [1] G.H. Fredrickson, *J. Chem. Phys.* **117**, 6810 (2002).
- [2] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).

Funding Acknowledgements

NNSA's Advanced Simulation and Computing (ASC), Physics and Engineering Model.