

Coarse-grained Modeling and Monte Carlo Study of Strain Induced Crystallization of Rubbers

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ABSTRACT

Strain induced crystallization (SIC) of rubbers is studied by Monte Carlo simulations using triangulated surface models with Gaussian bond potential. We find that the stress relaxation can be seen in the intermediate strain region or the two-phase coexistence region of amorphous and crystalline states. The obtained stress-strain curves are consistent with reported experimental data influenced by SIC. More interestingly, even when the rigid bonds are eliminated or replaced by empty bonds, the results remain almost the same. Not only rigid but also empty bond reduces the tensile energy of the amorphous state.

1. Introduction

Natural rubbers (NR) are widely used as industrial materials, but as complicated mechanisms are involved under large deformation, like strain induced crystallization (SIC) [1]. Though such rubbers have been studied for many years, further improvements are still of big interest.

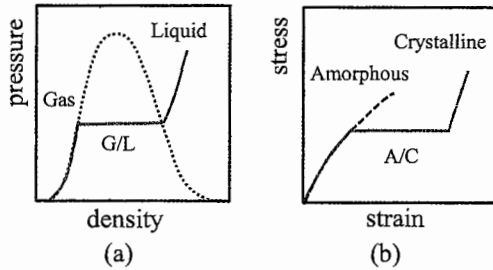


Fig. 1 (a) Pressure-density curve of gas-liquid transition, (b) the Clapeyron diagram of NR [1]

The SIC have been intensively studied, and the stress-strain (SS) curve, which corresponds to the intrinsic mechanical behavior, is experimentally clarified [1, 2]. The transition from amorphous to crystalline states can be compared with the gas-liquid transition (Fig. 1(a),(b)). Thus, SIC is considered to be universal in the sense that it has a plateau in the two-phase coexistence region. However, the crystallization ratio remains very low, and therefore, it is still controversial whether SIC shares such universal property of the first-order transition.

In this paper, we present triangulated surface models for SIC and show that the SS curves which are compatible with experimentally reported data influenced by SIC. The discrete 2D models are an extension of the triangulated surface model for membranes

(Figs. 2(a),(b),(c)). The models include new degree of freedom σ for crystallization of triangle edges or bonds (Figs. 2(d),(e),(f)). We examine two types of crystallization using this new variable σ ; "rigid" bond and "empty" bond.

2. Models

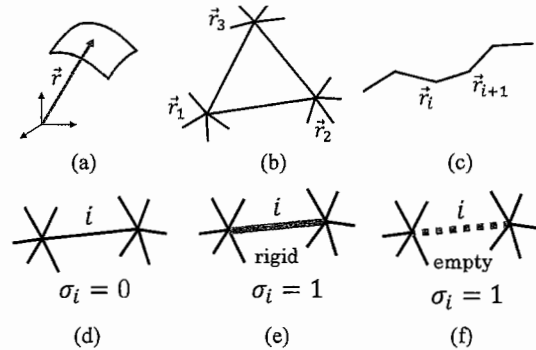


Fig. 2 (a) A triangulated surface in \mathbf{R}^3 , (b) a triangle, (c) a linear chain. Illustrations of (d) flexible, (e) rigid, and (f) empty states of bond i .

The Gaussian bond potential S_1 is defined by the sum of the bond length squares of triangles such that

$$S_1 = \sum_{ij} \ell_{ij}^2, \quad \ell_{ij} = |\vec{r}_j - \vec{r}_i|, \quad (1)$$

where $\vec{r}_i \in \mathbf{R}^3$ is the vertex position. This potential is exactly the same as that of the one-dimensional chain model for polymer (Fig. 2(c)). The only difference is whether the lattice is a chain or a triangle mesh. The one-dimensional chain model is mathematically well-established such that for all random distribution of points $\vec{x}_i (i = 1, \dots, n)$ the distribution of the sum $\sum_i \vec{x}_i$ becomes Gaussian $\exp[-\gamma(\sum_i \vec{x}_i - \langle \vec{x} \rangle)^2]$, where $\langle \vec{x} \rangle$ is the mean value of \vec{x}_i . Since $\sum_i \vec{x}_i$ is understood to be the vector from \vec{x}_1 to \vec{x}_n , the S_1 in Eq. (1)

is meaningful if $\sum_i \vec{x}_i$ is identified with $\vec{r}_{i+1} - \vec{r}_i$. This is the reason why we call the model, defined by S_1 in Eq. (1), "coarse-grained".

We introduce a new variable $\sigma_i (\in \{0, 1\})$ to define the crystalline state on the bond i . Here we assume that the bond i belongs to one of two different states; crystalline and flexible or amorphous. This can be expressed by

$$\sigma_i = 0 \text{ (amorphous)}, \quad \sigma_i = 1 \text{ (crystalline)}. \quad (2)$$

We should note that the value of σ for each state is changeable such that $\sigma_i = 0$ (crystalline) and $\sigma_i = 1$ (amorphous). The bond i in this crystalline state ($\Leftrightarrow \sigma_i = 1$) of Eq. (2) is assumed to be a rigid line of fixed length ℓ_0 moving by 3D translation and rotation.

Using this variable σ_i and the vertex position \vec{r}_i , we define the Hamiltonian $S(\vec{r}, \sigma)$ such that

$$\begin{aligned} S(\vec{r}, \sigma) &= S_1(\vec{r}, \sigma) + \kappa S_2(\vec{r}) + U(\vec{r}, \sigma) \\ S_1(\vec{r}, \sigma) &= \sum_{ij} \ell_{ij}^2, \quad S_2(\vec{r}) = \sum_{ij} (1 - \vec{n}_i \cdot \vec{n}_j), \\ U(\vec{r}, \sigma) &= \sum_i U_i, \\ U_i &= \begin{cases} \infty & (\sigma_i = 1 \ \& \ \ell_i \neq \ell_0 \ \& \ \chi > R) \\ 0 & \text{(otherwise)} \end{cases} \end{aligned} \quad (3)$$

The sum \sum_{ij} in S_1 denotes the sum over all bonds ij , \vec{n}_i in S_2 is the unit normal vector of the triangle i , and $U_i(\sigma)$ is the constraint on the bond length according to the value of σ_i and its length ℓ_i . This $U_i(\sigma)$ prohibits ℓ_i from being $\ell_i \neq \ell_0$ for the crystalline state. This is the reason why S_1 implicitly depends on σ . The symbol χ in U_i is the crystallization ratio, which is defined by $\chi = N_{\text{rigid}}/N_B$, where N_{rigid} is the total number of rigid bonds, and N_B the total number of bonds. The constraint $\chi < R$ on χ is imposed by a number R . If R is fixed to $R=0$, the model is restored to the standard model without the crystallization. The empty bond model is obtained by replacing $\ell_i \neq \ell_0$ with $\ell_i > \ell_0$ in the potential U_i , and no bending energy is defined on the empty bond.

3. Results and Discussion

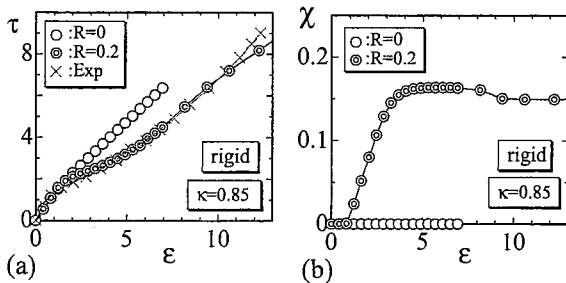


Fig. 3 (a) τ vs. ϵ with Exp [2] data, and (b) the crystallization ratio χ vs. ϵ of the rigid bond model.

The SS curves and χ of the rigid and empty models are plotted in Figs. 3 and 4 with Exp data, which are reported to be influenced by SIC [2]. This influence of SIC on Exp data is visualized in the stress

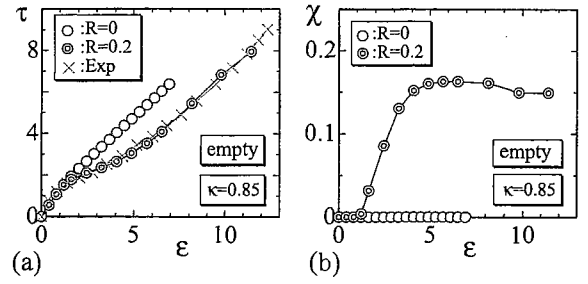


Fig. 4 (a) τ vs. ϵ with Exp [2] data, and (b) χ vs. ϵ of the empty bond model.

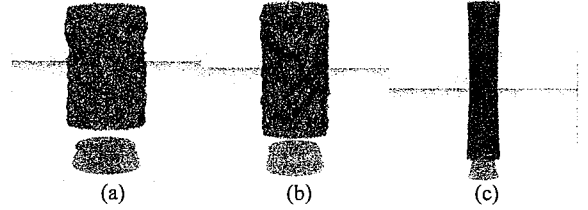


Fig. 5 Snapshots of cylindrical surfaces (a) $\chi=0.01$, (b) $\chi=0.05$, and (c) $\chi=0.16$.

vs. inverse-strain curves obtained by modified Mooney-Rivlin equation in [2]. Both of the numerical results in this paper are almost consistent with Exp data. In the snapshots in Figs. 5(a)-(c), the red small tube represents rigid bonds, which correspond to the crystalline state represented by $\sigma = 1$ and have no tensile energy contribution to S_1 .

In the case of FG modeling, we observed that experimental SS curves are also well reproduced numerically even though all bonds remain flexible [3]. The tensile energy of the bond ij in the FG model is typically given by $\gamma_{ij}(\sigma)\ell_{ij}^2$, where $\gamma_{ij}(\sigma)$ effectively plays a role of the tension coefficient. By taking the results of the rigid and empty bond models into consideration, we find that the same mechanism is shared by the FG model. This indicates that the strain relaxation is caused by a decrement of elastic energy, which allows the strain to be large, in the amorphous state. In the case of 3D empty bond model, the results will also be close to Exp data even in the largest strain region.

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References

- [1] P-A. Albouy and P. Sotta, In: Auriemma F., Alfonso G., de Rosa C. (eds) *Polymer Crystallization II. Advances in Polymer Science*, vol 277 (2015, Springer, Cham), 167–205.
- [2] S. Pradhan, F.R. Costa, U. Wagenknecht, D. Jehnichen, A.K. Bhowmick, G. Heinrich, *European Polymer Journal* 44 (2008), 3122–3132.
- [3] H. Koibuchi, C. Bernard, J-M. Chenal, G. Diguët, G. Sebald, J-Y. Cavaille, T. Takagi, and L. Chazeau, *Journal of Physics: Conf. Series* 1141 (2018), 012081(1-8).