Molecular Dynamics Simulation on cis-1,4 Polybutadiene under Cyclic Deformation: Chain Entanglements and Hysteresis

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ABSTRACT

Seeking for a new insight on hysteresis behaviors of rubber materials, we have performed several molecular dynamics simulations on polyethylene (PE) and polybutadiene (PB) under cyclic loading [1,2]. In the present study, we have first discussed the origin of initial residual stress, reported in [2], in the PB nano-block composed of 1000 random coil chains with average molecular mass of $[-CH_2-CH=CH-CH_2-]^{150}$. Here, the united atom approximation is applied for each methine (-CH=) and methylene (-CH$_2$-) center; we have adopted the potential function and parameters proposed by Gee and Boyd [3]. According to our previous approach, we have separately evaluated the stress for all the nodes, i.e. bond stretch, bending, torsion and van der Waals, finding out that the residual stress arises only on the bond stretch. Here, the PB chain has three different torsion nodes, -CH=CH-, -CH$_2$-CH$_2$- and =CH-CH$_2$-, so that it is insufficient to discuss the contribution of each node without considering the variation of spatial conformation. Thus we have evaluated the residual stress of bond stretch separately, by considering the possible three-dimensional conformation of $CH_2-CH_2-[CH=CH]-CH_2-CH_2$, $CH-CH_2-[CH_2-CH]=CH-CH_2$ and $CH=CH-[CH_2-CH_2]-CH=CH$. It reveals that the bonds belong to the cis-1,4 conformation, of which both ends has the conformation of "anticlinal" dihedral angle of CH$_2$-CH center, feel compressive stress while all the other bonds does tensile stress. We have referred to the configuration as "compression node".

Figure 1(a) shows the stress–strain response under cyclic elongation while Figs. 1(b)~(e) separated contribution of each nodes. As same as the PE case [1], the bond stretch and van der Waals dominate the hysteresis of the stress-strain curve of PB block; however, we have also find that compressive stress emerges on bending angles during the tension, leading subtle "strain softening" in the stress-strain response. This negative stress reversibly vanishes during the unloading process. We have then made further classification on the bond stretch hysteresis of Fig. 1(b), depending on whether the bond belongs to compression node or not. As shown in Fig. 1(f), only the compression nodes show hysteresis while
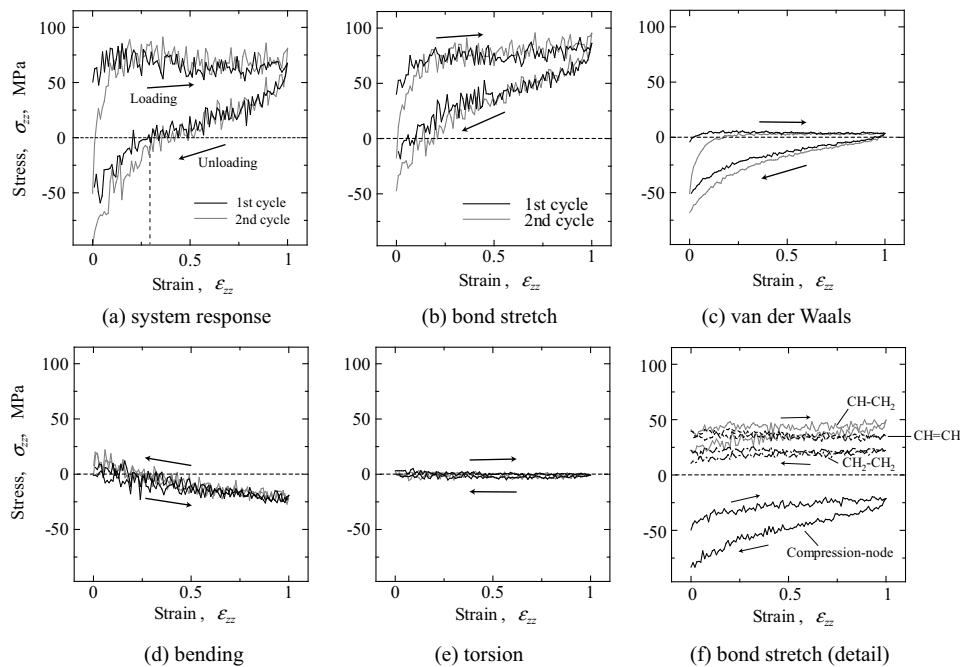
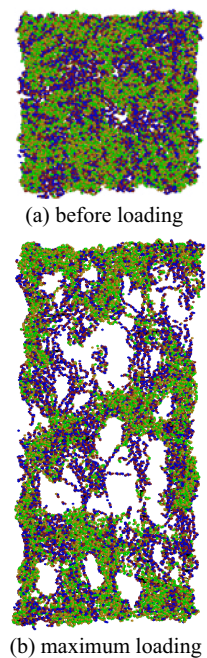Fig. 1   Stress–strain curves and separated components.

Fig. 2   Snapshots.

the other does almost constant tensile stress during the cyclic deformation. We have then visualized the distribution of compression nodes in Figs. 2(a) and 2(b), before loading and at the maximum strain of $\varepsilon_{zz} = 1.0$, respectively. In the figures, only a thin part of 2.0 nm width is extracted from the center of the PB block of 20 nm × 20 nm × 20 nm size. The light shaded parts indicate the compression nodes while the dark ones the other conformation. We can find that the compression nodes don't distribute uniformly but aggregate in the initial equilibrium (Fig. 1(a)). The structure show network-like morphology under large elongation, since the aggregated compression nodes don't fan out but the other nodes are straightened and oriented between them (Fig. 1(b)). From these results, we have led the following conclusions; (1) since compression nodes curl a molecular chain to small cluster, their aggregations work as "entanglement" since it is difficult for chains to sneak out each other, (2) the entanglements support the hysteresis, since the compression nodes have "margin" or "buffer" against tension, (3) the recovery of the bond compression in the aggregated cluster leads the compression on bending angle.

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