Quantitative Evaluation of Connectivity in Elastomers for Describing Rubber Elasticity Based on Network Theory

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In this review, the author introduces a recent contribution to the development of a quantitative evaluation method of connectivity in elastomers for describing rubber elasticity. In synthetic processes, the elastomers possess a heterogeneous network structure, which affects the rheological behaviors of elastomers, such as rubber elasticity. Although the heterogeneous structure of elastomers has been evaluated using both experimental and simulation methods, it is still difficult to estimate the heterogeneous structure of elastomers in terms of connectivity. Recently, the author reported a novel evaluation method for the chain connectivity of elastomers based on network theory to describe rubber elasticity. The unified centrality, including both topological and spatial information, can describe certain parameters related to rubber elasticity. Furthermore, the behavior of extended chains is also described by centrality. This approach is expected to contribute to progress in the theory of rubber elasticity by considering complex connectivity.

Key Words: Rubber elasticity / Network theory / Complex network science / Data science / Molecular simulation

1. BACKGROUND

1.1. Rubber elasticity in terms of network connectivity

Rubber elasticity is one of the rheological phenomena of elastomers in which network polymers in rubber states show unique behaviors such as large deformation, softness, and recovery of deformation compared with other solid materials. In the classical model of rubber elasticity, a Neo-Hookean solid is assumed to explain the mechanical properties of elastomers or gels under deformation, such as affine and phantom network models, where the deformation of a single polymer under deformation is assumed to be a Gaussian chain that determines the global stress\(^1\). With the progress of deformation, the stress suddenly shows an upturn because of the finite chain extensibility, which is explained using a non-Gaussian chain\(^2\). Recently, M. Zhong et al. reported that defects in the elastomer affect the elasticity in terms of both experiment and theory\(^6\). However, a rubber elastic model in terms of simple connectivity of polymer chains among cross-linking points in the network without the defects or dangling chains has not been well revealed due to the limitation of the quantitative evaluation methods of the connectivity.

1.2. Data science for complex system

Recently, data science has significantly contributed to the material science; this combination of the two sciences is recognized as materials informatics. Two major contributions can be considered: one is to find a new design or an optimized condition for the fabrication of materials, and the other is to understand the mechanism of the materials. Various data science approaches can deal with complex systems, such as multi-dimensional variations, non-linear phenomena, and complicated structures from the data. Therefore, it might be meaningful that the complex physical phenomena of materials, such as rheology, are tackled with data science. These data science approaches or methods can be divided into ‘black box’ and ‘white box’ methods. In black box methods, it is difficult for humans to determine the reason why the

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computer judges the results. Deep learning is a typical example of a black box method. It should be noted that recent development in explainable AI enables us to recognize the reasons for judgement by deep learning\(^7\). In contrast, white box methods are useful for extracting essential information from complicated relationships or messy structures, such as in sparse modeling, persistent homology, and network theory.

Network theory/analysis is a method in data science that is closely related to complex network science and graph theory. Network theory deals with graph or network structures, where nodes are connected by links. Network theory not only compares the structure between different networks but also extracts feature values in terms of connectivity for each node separately. There are several indicators to discuss the difference in the network structure, such as modularity, centrality, cluster coefficient, and degree coefficient. Therefore, these methods have been utilized in a wide range of areas in social science, biological science, infections, and so on. Recently, network theory has been applied to materials science\(^8\), where some essential parameters are extracted to represent the physical properties.

2. NETWORK THEORY FOR RUBBER ELASTICITY

2.1. Motivation

In this review, the author introduces a quantitative evaluation of the network structure of elastomers for describing rubber elasticity (Fig. 1). Although it is well known that the connectivity in elastomers significantly affects rubber elasticity, quantitative evaluation methods are limited. Thus, the network structure with heterogeneous connectivity is evaluated by closeness centrality, an indicator in network theory, and the effects of rubber elasticity, such as the distance between cross-linking points, fluctuation of cross-linking points, and formation of extended chains are investigated.

2.2. Network analysis of elastomers

Elastomers were prepared in a coarse-grained molecular dynamics simulation based on the OCTA/COGNAC simulator, because it is difficult to evaluate the connectivity in an experiment. To discuss only the effect of connectivity, the branching number of cross-linking points and bead number in a polymer chain between cross-linking points were unified to four and 22, respectively. As a homogeneous network, a diamond-like elastomer was constructed by mimicking the diamond structure, where carbon atoms and carbon-carbon bonds are cross-linking points and polymer chains. Synthetic polymers were prepared by cross-linking reactions of two types of 4-arm star polymers at the chain ends, such as tetra-PEG gel\(^10\). The cross-linking reactions were carried out at several concentrations \((c/c^*), c^*:\) overlap concentration)\(^\text{10}\). Because the reaction proceeded to more than 98 % with complementary reactions, these elastomers hardly have defects such as dangling and loop chains. In addition, a random network was prepared by exchanging the polymer chains with distance conditions (far, near, and random). Subsequently, all elastomers were shrunk to the same density \((\rho = 0.85)\), and uniaxial elongations were carried out.

Under uniaxial deformation, the stresses exhibited different behaviors over the elastomers. Affine deformation of the end-to-end distance, which is assumed in affine network models, clearly depends on the network structure, and merely the network prepared in \((c/c^*) = 3, \) and far and random conditions obeyed almost the affine deformation. However, the phantom network model, where the affine deformation was not assumed, could not explain the difference in the stresses, because the cross-linking density and branching number were unified in all elastomers. Thus, the difference in the

![Network structure of elastomers with (a) homogeneous and (b) heterogeneous connectivity. The sizes of cross-linking points correspond to the value of closeness centrality. Cross-linking points in the homogeneous network expand similarly within deviations, while those in the heterogeneous network tend to have uniqueness, which might be explained by network indicator such as closeness centrality. The figures were reproduced from the literature\(^11\).](image-url)
stress could be derived from the difference in the connectivity of polymer chains among the cross-linking points.

The connectivity of the elastomers was quantitatively analyzed using closeness centrality, which is one of the indicators in network theory. The closeness centrality is defined as the inverse of the sum of the shortest paths between a focusing node and other nodes (Fig. 2a). A typical example is shown in Fig. 2b-c. When the node is located at the center of the network, small values of the shortest paths afford high closeness centrality (Fig. 2b). In contrast, the closeness centrality located outside the network is lower because the values of the shortest path increase (Fig. 2c). It should be mentioned that only topological features were extracted using the closeness centrality because the weight in each link was always one. Thus, we have developed a modified centrality that includes both topological and spatial information by introducing the inverse of the distance between cross-linking points before the elongations into the weight of the links (Fig. 3a). This feature could be useful for network structures where the real distance is significant.

2.3. Description of rubber elasticity by closeness centrality

Some parameters related to rubber elasticity were described by the modified centrality\(^\text{11}\). In the phantom network model, the end-to-end distance between cross-linking points \(r(\lambda)\) and fluctuation of cross-linking points \(MSD(\lambda)\) were parameters that determined the stress. Therefore, the relationships between the modified centrality and these parameters were plotted (Fig. 3b-c). In the case of the end-to-end distance, a linear increase was confirmed over the elastomers (Fig. 3b). In contrast, a monotonous decrease in the fluctuation of the cross-linking points was observed (Fig. 3c). It should be noted that these relationships were not confirmed in the diamond-like elastomer. These results indicate that the

**Fig. 2** (a) Definition of closeness centrality. Examples for estimation of closeness centrality for nodes located in (b) center and (c) outside the network. The calculation was applied to the part of network.

**Fig. 3** (a) Introduction of modified centrality with both topological and spatial information. The relationship between (b) distance between cross-linking points and (c) fluctuation of cross-linking points as a function of modified centrality. The lower figures were reproduced from the literature\(^\text{11}\).
cross-linking points in the center of the network and with a high initial distance between cross-linking points contributed to the stress. Thus, the cross-linking points play a role in the stress, as determined by the connectivity of polymer chains in the elastomers.

The upturn in the stress-strain curve is also important for rubber elasticity, which is related to the failure or toughness of the elastomers. Thus, the formation of stressed chains was also evaluated, where the stressed chains were defined in two ways (Fig. 4a). As shown in Fig. 4b (lower), the ratios of the stressed chains were well described by the closeness centrality, supporting that the polymer chains located in the center of the network tended to be stressed chains. Additionally, the behavior of stress concentration by the stressed chains was also confirmed through network theory. Thus, the network feature is useful for realizing the effect of connectivity on the formation of stressed chains\(^{12}\).

**3. SUMMARY**

The author demonstrated that network theory is useful for describing rubber elasticity in terms of heterogeneous connectivity\(^{11-13}\). The network position of each cross-linking point was quantitatively evaluated using closeness centrality.

Furthermore, some parameters related to rubber elasticity, such as end-to-end distance, fluctuation of cross-linking points, and ratio of the stressed chains, were linearly explained by the centrality. In future work, network analysis might be applied to more complicated structures in terms of connectivity, such as elastomers with different molecular weights between cross-linking points, hierarchical heterogeneous structures, and entanglements in elastomers. Furthermore, it is expected that data science methods could contribute to the understanding of the mechanism of rheological behavior of several materials.

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