Analysis of Mechanical Behavior of Polymers Using Molecular Chain Network Model*
(Effects of Molecular Weight Distribution and Ultra-Violet Degradation)

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A computational procedure for analyzing the deformation and fracture of solid polymers is developed based on a molecular chain model. In the model, the polymer solid is represented by a network of nonlinear elastic chains. Cellular automata modeling is employed to generate the network of polymer chains. Van der Waals and viscous forces acting on the chains are taken into account and are approximated to act at the nodal points of the network. A stiffness equation is derived by employing the principle of virtual work, in which geometrical nonlinearity due to a large deformation is considered. Slippage and scission of chains are also taken into consideration. The effects of molecular weight distribution and molecular chain scission due to UV-degradation are discussed.

Key Words: High Polymer Materials, Tensile Properties, Computational Mechanics, Network Model, Molecular Chain, Degradation

1. Introduction

Polymeric materials are easier to manufacture and their specific strengths are higher than those of metallic materials. Because of these advantages, polymeric materials are being used in several ways. Polymeric materials that have excellent mechanical properties are desired. Studies devoted to the mechanical properties of polymeric materials have been categorized as microscopic in macromolecular chemistry or macroscopic in continuum mechanics. However, the mechanical properties of polymeric materials are strongly dependent on structures between the micro- and macro-scales, that is, on meso-scale structures. For this reason, even if the mechanical properties of a molecular chain are improved by molecular design, it is not necessarily the case that the mechanical properties of the corresponding polymeric material are improved. Some studies apply molecular dynamics method to study the relationship between meso-scale structure and macro-scale mechanical properties. Examples of this include the study of the behavior of molecular chains between walls by Monte Carlo simulation(1), the relationship of the stress-strain curve and compression of an amorphous polymer(2), the study of the elongation of an amorphous polymer(3), and the structural explanation of tensile yielding of a crystalline polymer by lamella cluster(4). However, the understanding of the relationship between the meso-scale structure and macro-scale mechanical properties of polymeric materials is still insufficient. Therefore, the purpose of this study is to elucidate the relationship between meso-scale structures and mechanical properties to enable the design of excellent polymeric materials.

The main characteristics of polymeric materials are that they contain many long or short chains. Additionally, the chains are strongly entangled, as shown in Fig. 1 (a). We tried some attempts(5)–(7) to analyze the mechanical properties of polymeric materials using the molecular chain network model (Fig. 1 (b)). In this study, the mechanical analysis method is proposed using a network model by considering the scission of molecular chains, molecular chain entanglement, and van der Waals force. A procedure using cellular automata to generate several structures for a network of molecular chains is presented. Using this procedure, some models are prepared. The
molecular weight distributions of these models are different. Using the models, the effects of molecular weight distribution on mechanical properties are investigated. A network model is prepared to investigate the relationship between UV-degradation and mechanical properties. UV-degradation is modeled by cutting the molecular chains in the model. The results of simulations with models in which some molecular chains are cut are shown.

2. Modeling

2.1 Model of molecular chains

The network model (shown in Fig. 1 (b)) is composed of a group of molecular chains arranged on a grid. A segment (shortest molecular chains of the network model) is modeled by a mass-spring model (Fig. 2). The mass-spring model includes several atoms. A long molecular chain can be constructed by connecting the mass-spring models. The length of one grid side of the network model is defined as a segment.

The force generated in a segment \( f \) is obtained from rubber elasticity theory and is given by the following equation:

\[
 f = \left( \frac{kT}{l} \right) L^{-1} \left( \frac{L}{l^2} \right),
\]

where \( r \) is the average end-to-end distance, which corresponds to the length between bonded mass pairs, \( l \) is the length between the molecules which compose the molecular chain, and \( n \) is number of molecules in one segment.

The terms \( k \) and \( T \) are Boltzmann constant and absolute temperature, respectively. \( L^{-1}(x) \) is inverse Langevin function, represented as Eq. (2).

\[
 L(x) = \frac{d}{dx} \ln \left( \sinh \frac{x}{z} \right) = \coth x - \frac{1}{z}.
\]

The stiffness of a molecular chain \( (E) \) is represented as

\[
 E(l) = \frac{kT}{A_0} \left( \frac{3}{n^{1/2}} + \frac{27}{5n^{3/2}} l^2 + \frac{297}{35n^{5/2}} l^4 \right),
\]

where \( A_0 \) is the cross-sectional area of the molecular chain. Computational results of this study do not depend on \( A_0 \), because the force acting on a segment is equal to the product of \( E(l) \) and \( A_0 \).

2.2 Model of scission

When a segment is stretched to a critical length, the segment is assumed to break. It means chain scission. In the calculation, the scission is modeled by gradually decreasing the stiffness of the segment to zero.

2.3 Model of entanglement

When molecular chains are positioned as in Fig. 3, they are assumed to be entangled. When the forces to which molecular chains are subjected are equilibrated (Fig. 4), the entanglement is likely to become an inextricable knot. Therefore, large resistance is occurs at the entanglement. The resistance is modeled by connecting two molecular chains with one node (large, black circle). In this study, the node is called an entanglement point. When the equilibrium force is violated, molecular chains start to slip at entanglement points (Fig. 5 (a)). This slippage is modeled by changing the initial lengths. Part of the initial length of a segment with lower axial tension is shifted to a segment with higher axial tension. When the node reaches the entanglement point the node shifts to the other side across from the entanglement point (Fig. 5 (b)). When the end of a molecular chain reaches an entanglement point, the molecular chain scission is occurred to model a slippage of molecular chains (Fig. 5 (c)).
strength of van der Waals force is less than that of the chemical bond. However, it is important to prevent the overlap of nodes. Lennard-Jones potential (Eq. (4)) is used to calculate van der Waals force:

$$\phi_{LJ}(b) = 4\varepsilon \left[ \left( \frac{\sigma}{b} \right)^{12} - \left( \frac{\sigma}{b} \right)^{6} \right],$$

(4)

where $b$ is the length between nodes, and constants $\varepsilon$ and $\sigma$ are defined as $1.64 \times 10^{-21}$ J and 0.40 nm, respectively. Van der Waals force is applied between nodes.

3. Generation of Network Model

Polymers are polymerized in a solvating medium in a manufacturing process and are clumped together by Brownian motion. In this study, the network model is generated by the following method using cellular automata(9). The method is referred to as polymerization and clump.

At first, molecular chains are randomly arranged on a cubic lattice. The length of one side of the cubic lattice corresponds to the length of one segment. These chains begin reptation motion(10) under the following conditions: (1) The beginning of the molecular chain must move to its adjacent point and drag the rest of the chain. (2) The direction of the polymer’s movement is toward where the density of the segments is highest, as shown in Fig. 6. (3) If the location, toward which the molecular chain tends to move is already occupied, the chain must move in the di-
rection such that the density of the segments is the second highest. (4) If all adjacent points are already occupied by other polymers, the chain does not move in this step. (5) If the molecular chain stays at the same point during two steps, the beginning and end of this molecular chain are reversed. (6) If the front of the molecular chain meets the front of another molecular chain, these polymers are then polymerized. Figure 7 shows the generation process. A small, black point represents a node, a large, black point represents an entanglement point, and a white point represents an overlap point of the molecular chains.

4. Formulation

The mechanical analysis of network model is described in this section. The following equation describes the stiffness of the mass-spring model (Fig. 2) and is derived by using the principle of virtual work. In this equation, the effects of the bending deformation of the mass-spring model are not considered.

\[
\int E A \frac{d(\Delta u_\xi)}{d\xi} \delta (\Delta u_\xi) d\xi + \int \rho A \Delta \ddot{u}_\xi \delta (\Delta u_\xi) d\xi + \int \rho A \Delta \ddot{u}_\eta \delta (\Delta u_\eta) d\xi + P \Delta \theta \delta (\Delta u_\eta) \bigg|_1^{\xi} \bigg|_1 \bigg|_1 \bigg|_1
\]  

where \( E(\lambda) \) is the longitudinal elastic modulus of the molecular chain, \( A \) is the cross-sectional area of the segment, \( P \) is the axial force, and \( \rho \) is the density of the segment. The rotational angle is represented by \( \theta \). Nodal forces in the \( \xi \) and \( \eta \) directions are represented by \( \Delta P_\xi \) and \( \Delta P_\eta \), respectively. The increment of displacement in the \( \xi \) and \( \eta \) directions is represented by \( \Delta u_\xi \) and \( \Delta u_\eta \) respectively. The fourth term on the left-hand side is the effect of rotation of the segment; in other words, the ge-

![Image](a) Model A  
![Image](b) Model B  
![Image](c) Model C

Fig. 8 Network models and their distribution
In this study, the mass matrix, and damping force are considered. This energy loss is considered to be the resistance to elongation. This resistance is modeled by a damping force. In this study, the damping force is assumed to act at nodes. The Eq. (6) is rewritten by considering the damping effect and van der Waals force as

\[
([K] + [K_g]) \{\Delta u\} + [M] \{\Delta \dot{u}\} = \{\Delta F\} ,
\]

where \(u\) is the nodal displacement, \([K]\) is the stiffness matrix, \([K_g]\) is the term of geometric nonlinearity, \([M]\) is the mass matrix, and \(\Delta [F]\) is the outer force.

When a molecular chain is elongated, energy loss occurs. This energy loss is considered to be the resistance to elongation. This resistance is modeled by a damping force. In this study, the damping force is assumed to act at nodes. The Eq. (6) is rewritten by considering the damping effect and van der Waals force (\(\Delta F_{VDW}\)) as

\[
([K] + [K_g]) \{\Delta u\} + [c] \{\Delta \dot{u}\} + [M] \{\Delta \ddot{u}\} = \{\Delta F\} + \{\Delta V_{VDW}\} .
\]

The damping matrix \([C]\) is defined by the following equation using Rayleigh damping \(^{(11)}\):

\[
[C] = \mu_M [M] + \mu_K [K] .
\]

In this study, \(\mu_K\) is assumed to be zero for the purpose of simplification. Only the mass matrix is considered.

5. Model for Analysis

5.1 Concentration of network model

Figure 8 shows models which are generated by the procedure explained previously and their molecular weight distributions are also shown. The initial arrangement of molecular chains in models A, B, and C are the same, but, the generation times (calculation steps) are different. The generation time increases from model A to model C. For this reason, the number average molecular weights of the models, in other words, the higher-order structure of the models, are different, even if the molecular weights of the models are the same. The number average molecular weight increases from model A to model C. This means that the molecular chains are longer in model C. In the next step, the change from liquid to solid should be considered, because the generation step in the network model is assumed to take place in solution. Because the effects of van der Waals force and the damping force in the solid state are higher than in the liquid state, concentration occurs during the change in state from liquid to solid. In this process, the network model starts the concentration using Eq. (7), in which van der Waals force and the damping force are considered. This step is identified to find the equilibrium condition for the network model. Figure 9 shows the models after the concentration step. The structure of each model is different because of the difference in the average molecular weight.

5.2 Network model for ultra-violet degradation

When polymers are irradiated by ultra-violet ray, degradation of mechanical properties occurs due to the breakage of molecular chains. In this study, this degradation is modeled by cutting segments randomly in concentrated network models.

Network model D (Fig. 10(a)) is prepared. The model is not degraded. Some network models for investigating the effect of degradation on mechanical properties are prepared by cutting 2.5% ∼ 60% of segments in model D. Figure 10(b) and (c) shows these network models. The proportion of cut segments is represented by \(\delta\). Degradation models in which segments are cut are not in equilibrium. However, the non equilibrium state does not affect the mechanical properties because the difference in the potential energy between the non equilibrium state and the equilibrium state is small. In addition, relaxation occurs in the early steps of deformation (details of deformation are described in section 6). Hence, in this study, the relaxation steps in the degradation models are skipped.

Breakage of molecular chains by ultra-violet irradiation is a chemical reaction caused by ray energy. It is assumed that the chemical reaction follows Arrhenius equation. The extent reaction (number of molecular chains cut) \(S\) is represented by the following equation:
Fig. 10 Degraded network model (Model D)

\[ S = \exp(-jt) \]  

Irradiation time and the reaction velocity constant are represented by \( t \) and \( j \), respectively. The relationship between nondimensional time \((jt)\) and the proportion of cut segments \((\delta)\) is represented by the following equation:

\[ jt = \ln(1 - S)^{-1} = \ln(1 - \delta)^{-1} \]  

6. Results and Discussion

6.1 Conditions for analysis

In this simulation, network models are assumed to be polyethylene. The number of molecules in a segment \((n)\) is 10. The initial length of segments \((r)\) is 0.8 nm. The critical length of the segment is taken as 3 times as the initial length. Temperature \((T)\), time increment \((\Delta t)\), and strain rate \((\varepsilon)\) are assumed to be 300 K, \(1.0 \times 10^{-6}\) s and 5 [1/s], respectively.

The bottom part of the network model is fixed. The upper part is loaded by upward uniform displacement. Nominal stress is evaluated for the resistance of the upper part. The depth of the cross section of the network model for the calculation of nominal stress is assumed to be the initial length of one segment (0.8 nm).
6.2 Effect of molecular weight distribution

Figures 11 and 12 show the simulation results for models A and C, respectively. Figure 13 shows the stress-stretch ratio curves for models A to C. The stretch ratio is defined as the length of the model after deformation divided by the initial length of the model, and is represented by $\lambda$. From the deformation process of model A (Fig. 11), it is observed that some molecular chains gather together and create a concentrated region. Other molecular chains connect the concentrated regions. When the models are deformed, the molecular chains which connect the concentrated regions are mainly elongated. On the other hand, the shape of the concentrated regions, such as the concentrated area at the center of the model, changes, but the molecular chains in the concentrated area are seldom elongated. This tendency is also observed in model B and model C. These results of simulations show that the deformation of polymeric materials involves the local elongation of molecular chains which connect concentrated areas. More molecular chains are elongated in model C compared with model A and model B. Molecular chains are longer in model C than in model A. Therefore, many molecular chains are elongated, even if molecular chains in concentrated areas are elongated in model C, due to the increase in the number of molecular chains connected to the concentrated regions (for example, elongated molecular chains that are located at the left part of the concentrated area of the center of the model in Fig. 12(a)–(c)). The stress-stretch ratio curves (Fig. 13), indicate that when the number average molecular weight increases, from model A to model C, the tensile strength also increases. This tendency is in agreement with previous experimental results(12)–(14). Stress in each model decreases severely between stretch ratios 2 and 3. Although the models (A ~ C) are not broken completely at this point, they can sustain only small loads. Therefore, when a significant decrease in stress occurs, the points of each model are defined as rupture strain. When the number average molecular weight increases, the rupture strain also increases. If molecular chains become longer, the number of chains connecting to neighboring concentrated areas increases. Therefore, more molecular chains can be elongated, which means an increase in the number of molecular chains which can sustain a load. This phenomenon results in the increase of tensile strength and rupture strain. It is concluded from the simulations that longer molecular chains play an important role in determining mechanical properties.

6.3 Effect of degradation

Simulations to investigate the effect of chain breakage by irradiation with ultra-violet ray, and the correspond-
ing results using the network models are shown in Fig. 10. Figures 14–16 show the deformation process, for δ equal to 0, 0.025, and 0.60, respectively. Comparing the deformation process of no degradation i.e., no molecular chains are cut (Fig. 14), and the degradation model (δ = 0.025) in which a few molecular chains are cut (Fig. 15), no major differences are seen. However, parts of elongated molecular chains are different. These results indicate that in the early stages of degradation, if molecular chains which have the possibility to sustain the load are cut, other chains can sustain the load in place of the cut chains. Figure 16 shows the cutting of many molecular chains occurring in several areas of the model. The long molecular chains become short molecular chains. Short chains, which are generated by cutting long chains, can not transfer the deformation the way long molecular chains can. Therefore, the model (δ = 0.60) is broken, even if the models are subjected to a slight deformation.

Figure 17 shows the relationship between the irradiation time of ultra-violet ray and rupture strain. Rupture strain is almost constant until \( t \) equals \( 10^{-1} \), from which point it decreases rapidly. This tendency is similar to previous experimental results\(^{(15)}\). If elongated molec-
ular chains are broken by irradiation by ultra-violet ray, other non-elongated molecular chains sustain the load. Therefore, rupture strain does not decrease in the early stages of UV-irradiation. This description indicates that, when polymeric materials are elongated, molecular chains which connect the concentrated areas are mainly elongated. Molecular chains in the concentrated regions are seldom elongated. If molecular chains in concentrated regions are broken by UV-irradiation, this does not greatly affect rupture strain.

The reason for the rapid decrease in rupture strain after a certain amount of UV-irradiation is the breakage of molecular chains which are bearing loads or can bear loads. This implies the effacement of the load transmission by the molecular chains.

7. Conclusions

In this paper, the generation method of network models by cellular automata is presented. Simulations which assume the tensile test using network models with several average molecular weights are carried out. The simulated results of the relationship between the number average molecular weight and tensile strength are similar to experimental results. In addition, it was found that the deformation of polymeric materials is mainly due to the elongation of local molecular chains which connect neighboring concentrated areas. When the number average molecular weight increases, rupture strain also increases, and long molecular chains affect the mechanical properties. The effects of degradation on mechanical properties were investigated by cutting molecular chains in the model. The numerical results of the relationship between the irradiation time of ultra-violet ray and rupture strain are similar to experimental results. It is suggested that rupture strain does not decrease in the early stages of UV-irradiation, because non-elongated molecular chains start to sustain the load instead of molecular chains broken by UV-irradiation.

References


