Relaxation Behavior of Network Polymers with Random Connectivity

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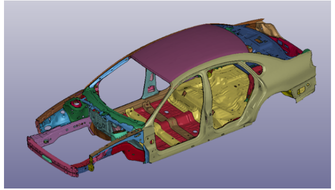
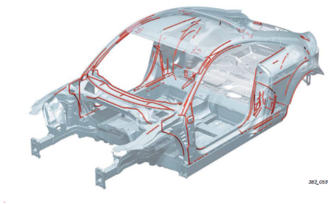
1. Introduction
   - Adhesive Bonding Technology as a Key to Multi-Materialization
   - Durability of Rubber
   - ゴムのモデル化

2. ランダムネットワークの検討
   - ランダムネットワークについて

Adhesive Bonding Technology



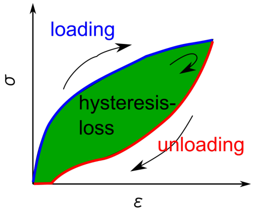


- For Energy conservation
  - weight reduction of cars
  - multi-materialization
  - adhesive bonding technology is a key
- durability in long-term use is important
  - Especially for fatigue tests
  - reliability of polymer materials is still ambiguous

1. focusing on Energy conservation
   - weight reduction of transportation equipment, especially automobiles is being considered.
   - for that purpose, multi-materialization using Aluminum, Magnesium, CFR(T)Ps is discussed.
   - these different colors
   - in the process, adhesive bonding technology is a big key.
   - for example, these red lines
2. requirements for network polymers used as adhesives are
   - not only high primary mechanical properties
   - but also the ability to withstand fatigue tests
   - , in which the polymer is repeatedly deformed at various deformation rates in order to ensure durability in long-term use.

Mechanical Hysteresis Loss and Fracture Energy

- Mechanical Hysteresis Loss
  - Reduced stress on unloading
  - Energy dissipation during cycle
  - Possitive correration with fracture energy[a]
- The origin of Hysteresis Loss[b]
  - Viscoelastics
  - Crystallization
  - Derived by added filler



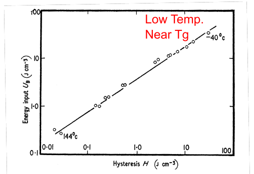


Fig. 1.—Energy input at break U_B against hysteresis H at break for SBR gum vulcanizate over a temperature range of −40 to 144° C.

[a] K.A.Grosch, J.A.C.Harwood, A.R.Payne, Rub. Chem. Tech., 41, 1157(1968)

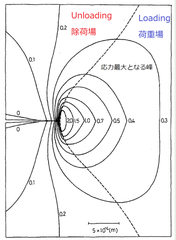
[b] A.R.Payne, J.Poly.Sci.:Sympo., 48, 169(1974)

- hyst
  - Mechanical Hysteresis is illustrated in this figure.
  - Reduced stress comes out on unloading compared with loading one.
  - this green area is equivalent to Energy dissipation during cycle
  - and the intensity of hysteresis loss had been reported to have Possitive correration with fracture energy by Payne.
- The origin of hysteresis loss is also categorized by Payne
  - Viscoelasticity based
  - Crystallization
  - Derived by added filler

Andrews Theory for Rubber Toughness

Andrews Theory

- Focused on stress field around the crack[a]
  - Stress Loading field and Unloading one
- On the progress of the crack, stress field is transit
  - Hysteresis Loss⇒Energy Dissipation
  - Surpress the progress of Crack



[a]E.H.Andrews, Y.Fukahori, J. of Mat. Sci. 12, 1307 (1977)

疲労破壊も考慮すると

- 可逆的であることが望ましい。$\neq$ 犠牲結合
- 変形の周期に対応できるように、回復速度も重要。
- 粘弾性挙動としてのヒステリシスロス ⇔ 緩和挙動

- On the fracture of rubber, Andrews proposed a model focused on Stress fields around the Crack top area
- stress fields can be divide in twe regions, stress loading field and unloading one.
- On the progress of the crack, stress field is transit
  - Hysteresis Loss⇒Energy Dissipation
  - Surpress the progress of Crack

Classical Theory of Rubber Elasticity

Free Energy Density of Rubbers against Strain invariant

$$\frac{F}{V} = W = C_0 + \underbrace{C_1(I_1-3) + C_2(I_2-3)}_{Mooney-Rivlin Model} + \sum_{i,j=1}^{\infty} C_{ij}(I_1-3)^i(I_2-3)^j$$

Neo-Hookean Model

$W = C_1(I_1 - 3)$

against Uniaxial elongation

$$\sigma_{nom} = 2C_1\left(\lambda - \frac{1}{\lambda^2}\right) = G\left(\lambda - \frac{1}{\lambda^2}\right)$$

Mooney-Rivlin Model

$W = C_1(I_1 - 3) + C_2(I_2 - 3)$

against Uniaxial elongation

$$\sigma_{nom} = 2\left(C_1 + C_2\frac{1}{\lambda}\right)\left(\lambda - \frac{1}{\lambda^2}\right)$$

With or without Junction Points fluctuation

Affine Network Model [a]

$G_{affine} = \nu k_B T$

ν: Number density of strands in the system

[a] P.J. Flory, Principles of Polymer Chemistry, (1953)

Phantom Network Model [a]

$$G_{phantom} = \nu k_B T\left(1 - \frac{2}{f}\right)$$

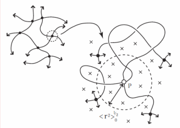
f: Functionality of Junction Points

[a] H.M. James, E.J. Guth, Chem. Phys., 21, 6, 1039 (1953)

Constraint Factors for Junction Points and Strands

Vicinity of Junction Point

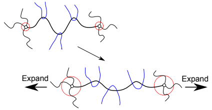
- Junction points are surrounded by many of adjacent strands(x in fig.).
- Fluctuation of junctions are suppressed.



combination of G_c and G_e

- Constrained Junction Model
  - Constraints are reduced and G approaches to G_c.[a]
- Topological relationships
  - Contribution of entanglement.[b]

$$G_e = T_e G_N^0$$



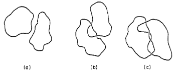


Figure 4. Three topological relationships between two closed loops: (a) not entwined, (b) once entwined, (c) twice entwined.

[a] P.J.Flory, J.Chem.Phys., 66, 12, 5720 (1977)
[b] D.S.Pearson and W.Graessley, Macromol., 11, 3, 528 (1978)

Constraint Factors for Junction Points and Strands

- Diffused-Constraint Model
  - Confining potential affect all points along the chain.[a]
- Nonaffine Tube Model
  - Improved model of "Edwards' Tube Model".[b]
- Slip-tube Model
  - A pairwise interaction of chains is introduced.[c]

- allowframebreaksbbb
- bbbb
- Z

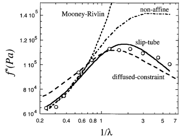
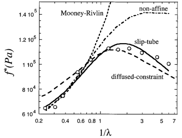


Figure 5. Fit of the data by Pak and Flory[20] on cross-linked poly(dimethylsiloxane) (open circles) by the diffused-constrained model (dashed line), Mooney−Rivlin expression (dotted line), nonaffine tube model (dash−dotted line), and the slip-tube model (solid line).

[a] A. Kloczkowski, J.E. Mark, B. Erman, Macromol., 28, 5089 (1995)
[b] M. Rubinstein, S. Panyukov, Macromol., 30, 25, 8036 (1997)
[c] M. Rubinstein, S. Panyukov, Macromol., 35, 6670 (2002)

Recent approach for Constraints (Entanglements)

- Diffused-Constraint Model
  - Confining potential affect all points along the chain.[a]
- Nonaffine Tube Model
  - Improved model of "Edwards' Tube Model".[b]



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ランダムネットワークの検討

- 前述のモデルの問題点
  - 変形速度依存性の議論が陽に行われていない。
  - 基本となる PNM の再現が必須。
- ネットワーク構造の連結性にランダム性を導入
  - Flory のファントムネットワークの要件に合致 [a]
    - the mean values $\bar{\boldsymbol{r}}$ of starand fluctuate
    - fluctuations $\Delta \boldsymbol{r} = \boldsymbol{r} - \bar{\boldsymbol{r}}$ are Gaussian
    - the mean-square fluctuations depend only on structure
- Previous Work for Random Network
  - Random end-crosslink for telechelic polymers[b]
  - Primitive Chain Network Simulation[c]

[a] P. J. Flory, Proc. R. Soc. London. Series A, 351, 351 (1976)
[b] G.S. Grest, et.al., Non-Cryst. Solids, 274, 139 (2000)
[c] Y. Masubuchi, Nihon Reoroji Gakkaishi, 49, 2, 73 (2021)