Relaxation Behavior of Network Polymers with Random Connectivity

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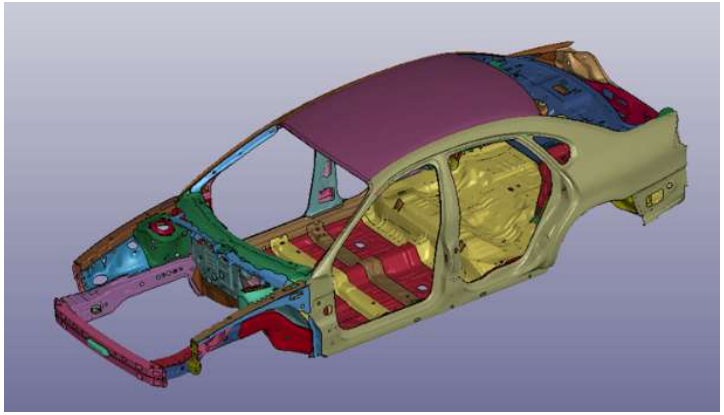
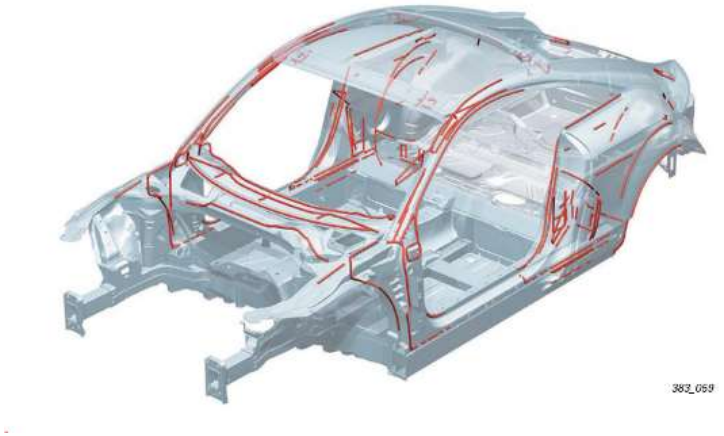
1 Introduction
- Adhesive Bonding Technology as a Key to Multi-Materialization
- Theoretical Models for Rubber
- Objectives

2 Simulation
- Generation Recipe of Random Networks
- Phantom and KG Chains as Strands
- Simulation Conditions

3 Results
- Networks with Phantom Chains
- KG Chain Networks
- Relaxation in KG Networks

Adhesive Bonding Technology

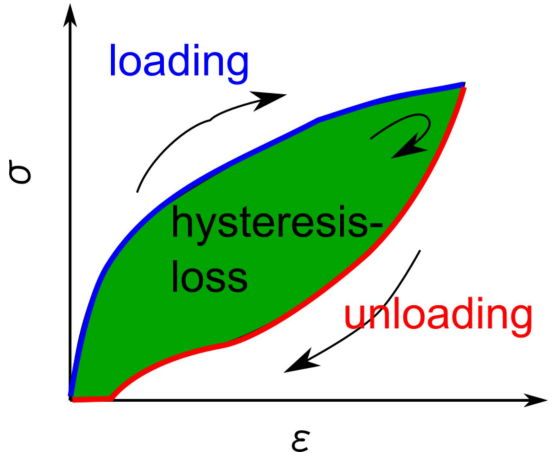




- For Energy conservation
  - weight reduction of cars
  - multi-materialization
  - adhesive bonding technology is a key
- durability in long-term use is important
  - Especially for alertfatigue tests
  - reliability of polymer materials is still ambiguous

Mechanical Hysteresis Loss and Fracture Energy

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



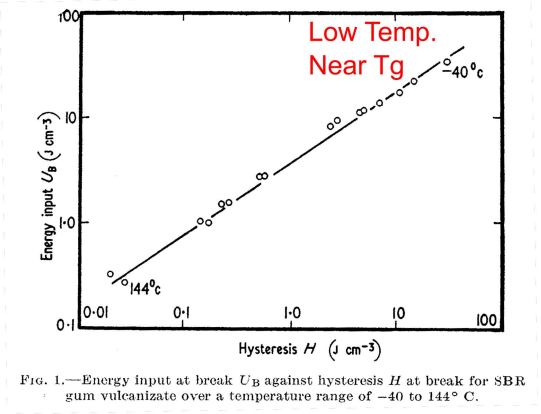


FIG. 1.—Energy input at break U_B against hysteresis H at break for SBR gum vulcanizate over a temperature range of −40 to 144° C.

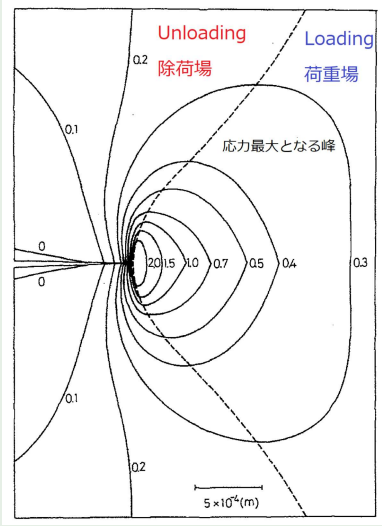
[a] K.A.Grosch, J.A.C.Harwood, A.R.Payne, Rub. Chem. Tech., 41, 1157(1968)

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

Andrews Theory for Rubber Toughness

Andrews Theory

- Focused on stress field around the crack[a]
  - Stress Loading zone
  - Unloading one
  - divided by stress maximum line
- On the progress of the crack,
  - stress field is transit
  - Hysteresis Loss⇒Energy Dissipation
  - The progress of Crack is Suppressed
- Bigger Hysteresis Loss results in Higher Toughness.



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

Classical Theory of Rubber Elasticity

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 Poinits 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]

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

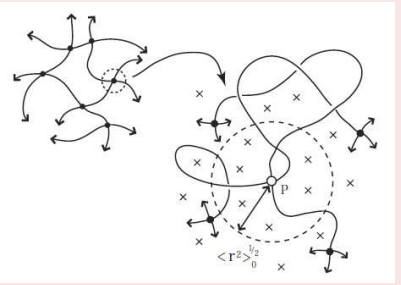
f: Functionality of Junction Points

[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.



Effect of other strands (Combination of G_c and G_e)

- Suppress the fluctuation of Junction Point
  - Deviate from Phantom Network Model and higher G_c
- Strands Entangles each other
  - Works as a Junction Point
  - Generate additional G_e

Storage modulus G is combination of G_c and G_e

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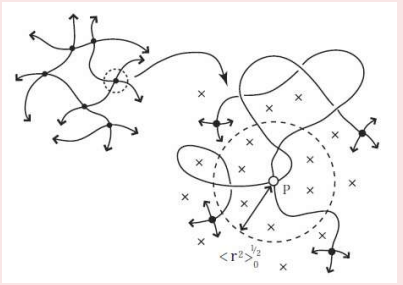
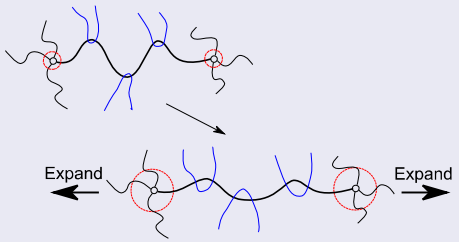


Effect of other strands (Combination of G_c and G_e)

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

$$G_e = T_e G_N^0$$



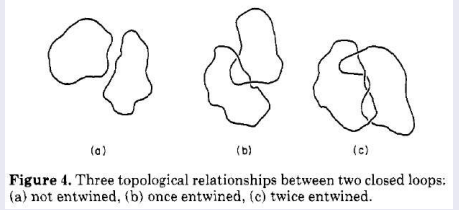


Figure 4. Three topological relationships between two closed loops: (a) not entwined, (b) once entwined, (c) twice entwined.

[a] P.J.Flory, J.Chem.Phys., 66, 12, 5720 (1977)

[b] D.S.Pearson and W.Graessley, Macromol., 11, 3, 528 (1978)

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]
- Slip-tube Model
  - A pairwise interaction of chains is introduced.[c]

[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)

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$$f^*(\lambda^{-1}) = G_c + \frac{G_e}{0.74\lambda + 0.61\lambda^{-1/2} - 0.35}$$

$$G_c = \nu k_B T \left(1 - \frac{2}{\phi}\right), \quad G_e = \frac{4}{7}\nu k_B T L$$

where ν is the number density of network chains,
L is the number of slip-links per network chain

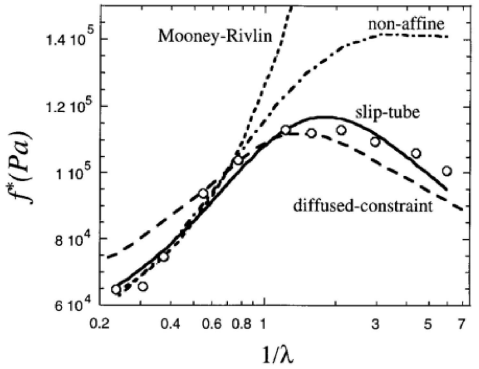
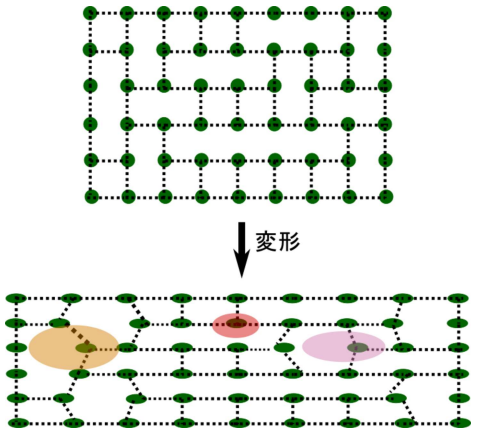


Figure 5. Fit of the data by Pak and Flory[20] on cross-linked poly(dimethylsiloxane) (open circles) by the diffused-constrained model (dashed line), Mooney–Rivlin expression (dotted line), nonaffine tube model (dash–dotted line), and the slip-tube model (solid line).

[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)

Random Networks as a key for PNM

- Introduction of Random Connectivity.
- Criteria for PNM is fulfilled[a].
  - the mean values $\bar{r}$ of strands are 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 endcrosslink for telechelics[b]
  - Primitive Chain Network Simulation[c]



[a] P. J. Flory, Proc. R. Soc. London. 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)

Objectives

- Recent approach for rubber elasticity models are based on Phantom Network Model.
- Introducing random connectivity, MD simulation studies were carried out.
- To investigate the criteria for Phantom Network Model, Two model chains are used.
  1. Employing phantom chain, basics for PNM is examined.
  2. Changing the chain to KG Chain, constraints effects are investigated.
     - Excluded Volume Effect
     - No mutual crossing of Strands

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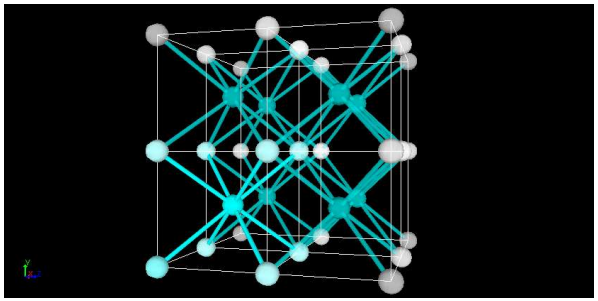
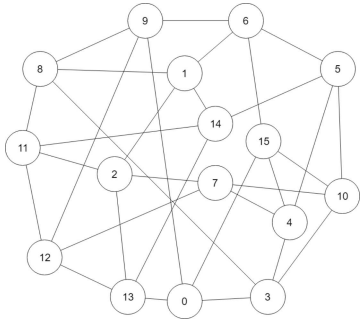
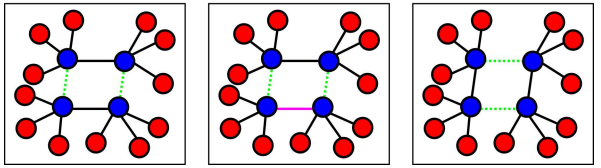
Generation of Initial Structure of Random Networks

1. 8-Chain Model is used as starting structure in Real space.
   - Randomly selected edge is removed until desired functionality.
   - Topological model is generated.
2. Randomness is introduced in topological space.
   - By edge exchange, random connectivity is introduced for each node.
3. Corresponding real space structure is generated.
4. According to e2e distance of strand, system size and multiplicity are set.





- 初期状態は、黒色のボンドと潜在的な緑色のボンド（8-Chain のときに存在）
- 任意のボンド（ピンクのボンド）を一つ選択：真ん中の状態
- そのボンドを含んだ平行四辺形のトポロジーを探す。
- 二本毎にセット（黒色のボンドと緑色のボンド）で入れ替える。



Phantom and KG Chains as Strands

- Phantom Chain:
  - No Excluded Volume is set (no segmental interaction).
  - "Force Cap LJ" is set as Angle Potential to enumerate e2e length of KG Chains.
  - Harmonic bond (k=1000)
- KG Chain:
  - Excluded Volume is set by Repulsive LJ Potential.
  - Bond Potential is set to FENE.
  - Because of above two potentials, No Chain crossing will occur.

Reluxation of Initial Structure in KG Network

KG Network: KG chain as strand

- Relaxation of initial structure is important.

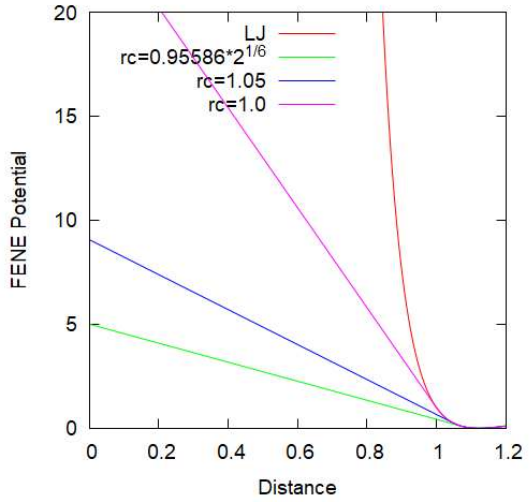
$$U_{KG}(r) = \begin{cases} U_{nonbond} = U_{LJ} \text{ where } r_c = 2^{(1/6)}\sigma \\ U_{bond} = U_{LJ} + U_{FENE} \end{cases}$$

Initial Structure Relaxation

- According method of Auhl[a]
  - Using force-capped-LJ pot.
  - relaxed by Slow Push Off

$$U_{FCLJ}(r) = \begin{cases} (r - r_{fc}) * U'_{LJ}(r_{fc}) + U_{LJ}(r_{fc}) & r < r_{fc} \\ U_{LJ} & r \geq r_{fc} \end{cases}$$

[a] R. Auhl et al. J. of Chem. Phys., 119, 12718 (2003)



- force-capped-LJ Pot.
- gradually entangled