Relaxation Behavior of Network Polymers with Random Connectivity

Hiroshi Sasaki

Toagosei Co., Ltd.

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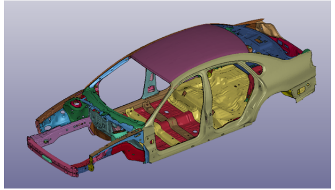
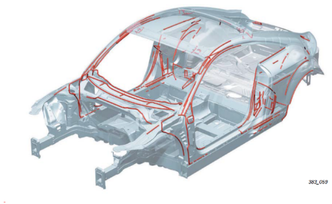
Adhesive Bonding Technology





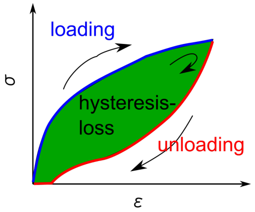
- For Energy conservation
  - weight reduction of cars
  - multi-materialization
  - adhesive bonding technology is a key
- durability in long-term use is important
  - Especially for fatigue tests
  - reliability of polymer materials is still ambiguous

Let me start with this slide as background.

1. focusing on Energy conservation
   - weight reduction of cars is big issue.
   - 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
  - Positive correlation with fracture energy[a]
- The origin of Hysteresis Loss[b]
  - Viscoelastics
  - Crystallization
  - Derived by added filler



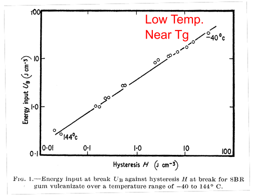


FIG. 1.—Energy input at break U_B against hysteresis H at break for SBR gum vulcanizate over a temperature range of −40 to 144° C.

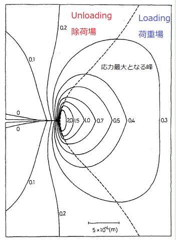
[a] K.A.Grosch, J.A.C.Harwood, A.R.Payne, Rub. Chem. Tech., 41, 1157(1968)
[b] A.R.Payne, J.Poly.Sci.:Sympo., 48, 169(1974)

- hyst
  - Mechanical Hysteresis is illustrated in this figure.
  - this green area is equivalent to Energy dissipation during cycle
  - Positive correlation with fracture energy had been reported to have 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 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



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

- 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 zone and unloading one.
- On the progress of the crack,
  - stress field is transit
  - During this transition, Hysteresis Loss is occur and dissipate energy
  - through this process, the progress of Crack is suppressed

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)

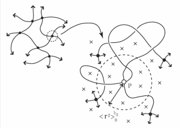
Here, the classical theories of rubber Elasticity are summerized.

- Considering junction points fluctuation, Phantom Network Model is proposed.
- in this model, Modulus is reduced depending on the functionality of junctions.

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

- Suppress the fluctuation of Junction Point
  - Deviate from Phantom Network Model
  - Affect 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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- Previous models
  - On the uniaxial deformation, constraints are released and G approaches to G_c
  - Considering topological effect can be counted as Ge

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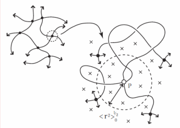
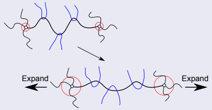


Effect of other strands

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

$$G_e = T_e G_N^0$$



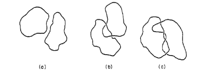


Figure 4. Three topological relationships between two closed loops: (a) not entwined, (b) once entwined, (c) twice entwined.

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

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

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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]

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[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

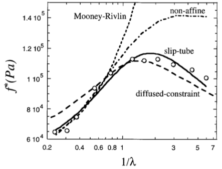
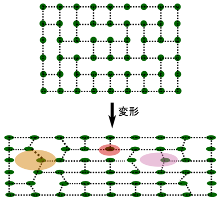


Figure 5. Fit of the data by Pak and Flory[20] on cross-linked poly(dimethylsiloxane) (open circles) by the diffused-constrained model (dashed line), Mooney−Rivlin expression (dotted line), nonaffine tube model (dash−dotted line), and the slip-tube model (solid line).

[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

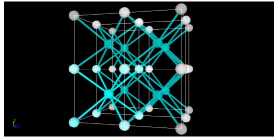
- Introduction of Random Connectivity.
- Criteria for PNM is fulfilled[a].
  - the mean values $\bar{\boldsymbol{r}}$ of strands are fluctuate
  - fluctuations $\Delta \boldsymbol{r} = \boldsymbol{r} - \bar{\boldsymbol{r}}$ are Gaussian
  - the mean-square fluctuations depend only on structure
- Previous Work for Random Network
  - Random endcrosslink for telechelics[b]
  - Primitive Chain Network Simulation[c]

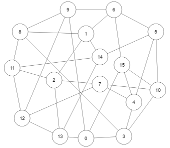


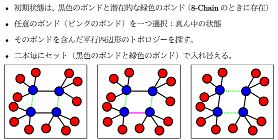
[a] P. J. Flory, Proc. R. Soc. London. A, 351, 351 (1976)
[b] G.S. Grest, et.al., Non-Cryst. Solids, 274, 139 (2000)
[c] Y. Masubuchi, Nihon Reoroji Gakkaishi, 49, 2, 73 (2021)

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.







Reluxation of Initial Structure in KG Network

KG Network: KG chain as strand

- Relaxation of initial structure is important.

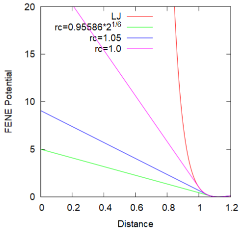
$$U_{KG}(r) = \begin{cases} U_{nonbond} = U_{LJ} \text{ where } r_c = 2^{(1/6)}\sigma \\ U_{bond} = U_{LJ} + U_{FENE} \end{cases}$$

Initial Structure Relaxation

- According method of Auhl[a] に従い、
    - 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

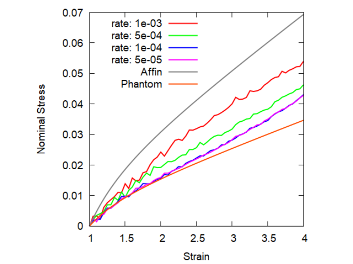
「素抜け鎖」の力学応答

「素抜け鎖」でのランダムネットワーク

- 「排除体積効果および絡み合いのない」ネットワーク

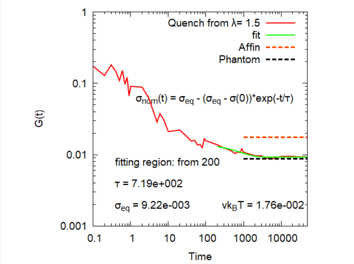
一軸伸張結果

- 伸張速度低下で
  ファントム応答に漸近



ステップ変形の応力緩和

- 高速伸長：$\dot{\gamma} = 1e^{-3}$
- 変位：$\lambda = 1.5$



Strand length Effect for 4-Chains

- Strand length is varied from 36 to 48
- System size is reduced to keep $\rho = 0.85$

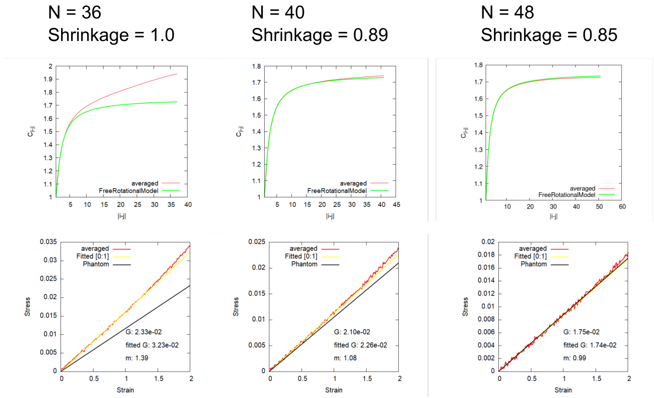


Figure: Strand Length Comparison for N = 36, 40, 48

Comparison of Functionality (f = 3, 4, 6)

f = 3	f = 4	f = 6
N = 48	N = 48	N = 48
multi = 4	multi = 3	multi = 2

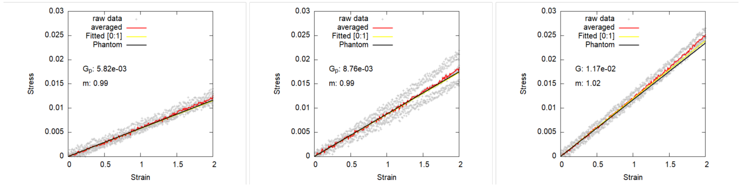


Figure: Comparison of Functionality (f = 3, 4, 6)

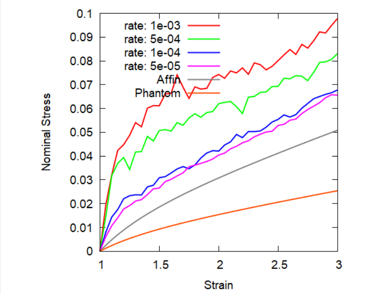
KG 鎖の力学応答

KG 鎖の四分岐ランダムネットワーク

LJ ポテンシャルによる排除体積効果および絡み合い

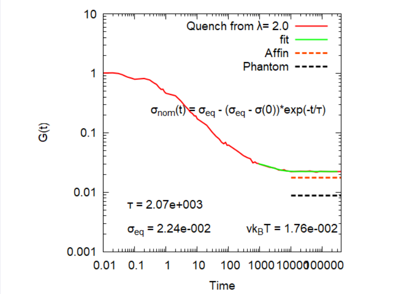
一軸伸張結果

- ネオフッキアンに漸近
- ANM よりも応力は高い

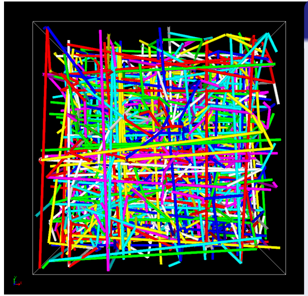


応力緩和関数 $G(t)$

- ステップ変形（$\lambda = 2.0$）
- ANM よりも高弾性率



Analysis of Entanglements in Network: Z1-code



Comparison with Homopolymer Melt

- Z is number of entanglements per chain

	Homo	4 Chain NW
Segments	50	48
Chains	200	768
Entanglements	204	800
Entangled Chains	134	557
$< Z >_{Z1}$	1.02	1.04

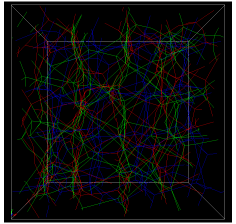
Z1-code?

- Algorism to visualize and count entanglements[a]

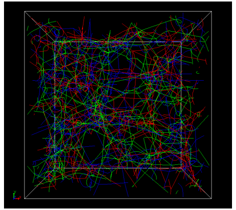
[a] M. Kröger, Comput. Phys. Commun. 168, 209 (2005)

Reduced Entanglements by NPT Model

- 4-Chain-NPT

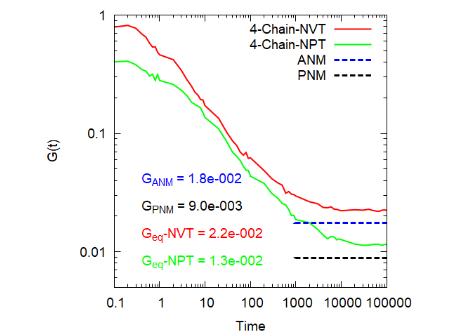


- 4-Chain-NVT



$G(t)$

- Step Deformation $(\lambda = 2.0)$
- Reduced Modulus



Entanglement effect in Slip-tube Model

Entanglement in Slip-tube Model

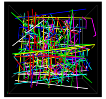
Theoretical model by Rubinstein[a]

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

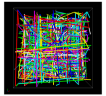
and L is the number of slip-links per network chain

[a] M. Rubinstein, S. Panyukov, Macromolecules, 35, 6670 (2002)

NPT
(less Entgld.)



NVT
(well Entgld.)



Ensemble	NPT	NVT
Chains, ν	768, 0.018	
$G_c = \nu \times (1 - 2/4)$	0.009	
Entanglements	278	800
Entangled Chains	249	557
L	278/768=0.36	800/768=1.04
$G_e = 4/7 \times \nu \times L$	0.004	0.011
$G_{calcd.} = G_c + G_e$	0.013	0.020
$G_{measd.}$	0.013	0.022

aa