Relaxation Behavior of Network Polymers with Random Connectivity

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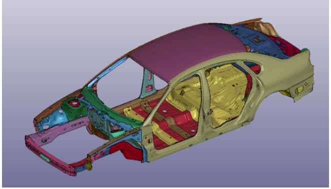
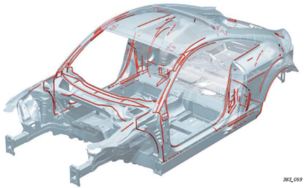
Adhesive Bonding Technology

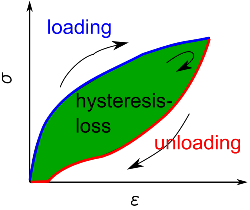




- For Energy conservation
  - weight reduction of cars
  - multi-materialization
  - adhesive bonding technology is a key
- durability in long-term use is important
  - Especially for alertfatigue tests
  - reliability of polymer materials is still ambiguous

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



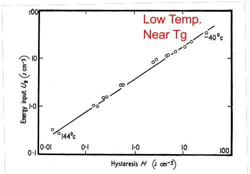


FIG. 1.—Energy input at break U_B against hysteresis H at break for SBR gum vulcanizate over a temperature range of −40 to 144° C.

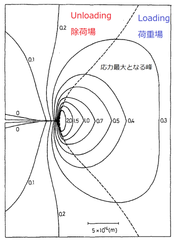
[a] K.A.Grosch, J.A.C.Harwood, A.R.Payne, Rub. Chem. Tech., 41, 1157(1968)

[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]

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

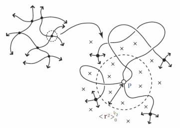
f: Functionality of Junction Points

[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

Constraint Factors for Junction Points and Strands

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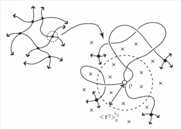
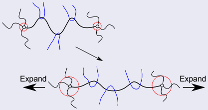


Effect of other strands (Combination of G_c and G_e)

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

$$G_e = T_e G_N^0$$



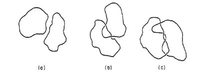


Figure 4. Three topological relationships between two closed loops: (a) not entwined, (b) once entwined, (c) twice entwined.

[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

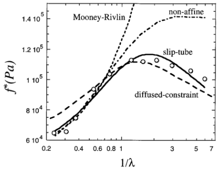
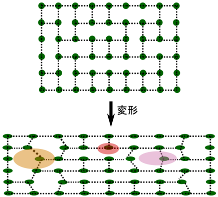


Figure 5. Fit of the data by Pak and Flory[20] on cross-linked poly(dimethylsiloxane) (open circles) by the diffused-constrained model (dashed line), Mooney−Rivlin expression (dotted line), nonaffine tube model (dash−dotted line), and the slip-tube model (solid line).

[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 $\bar{\boldsymbol{r}}$ 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]



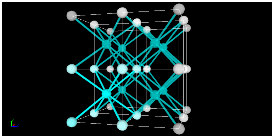
[a] P. J. Flory, Proc. R. Soc. London. A, 351, 351 (1976)
[b] G.S. Grest, et.al., Non-Cryst. Solids, 274, 139 (2000)
[c] Y. Masubuchi, Nihon Reoroji Gakkaishi, 49, 2, 73 (2021)

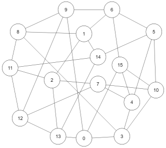
Objectives

- 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

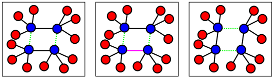
Generation of Initial Structure of Random Networks

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.

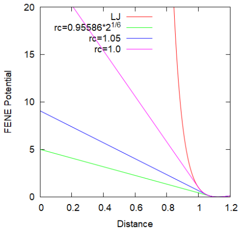
$$U_{KG}(r) = \begin{cases} U_{nonbond} = U_{LJ} \text{ where } r_c = 2^{(1/6)}\sigma \\ U_{bond} = U_{LJ} + U_{FENE} \end{cases}$$

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

Strand length Effect for Phantom Chain NW

- Strand-length is varied from 36 to 48 for f=4
- System size is reduced to keep $\rho = 0.85$

N = 36
Shrinkage = 1.0

N = 40
Shrinkage = 0.89

N = 48
Shrinkage = 0.85

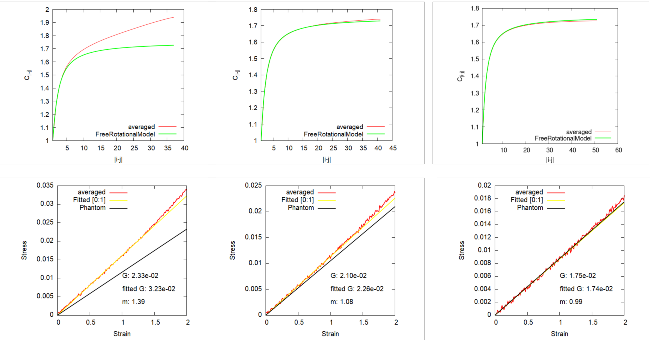


Figure: Strand Length Comparison for N = 36, 40, 48

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

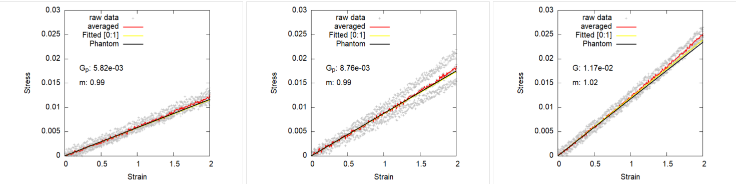


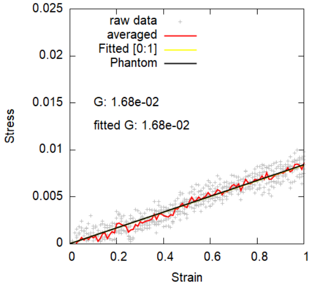
Figure: Comparison of Functionality ($f = 3, 4, 6$)

Mechanical Responce for KG Chains(f=4, N=48)

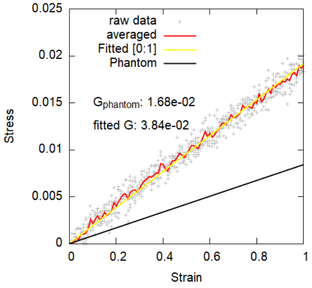
4-Chain Random Network with KG Chain

- Excluded Volume Effect by non-bonding LJ Potential.
- No strands mutual crossing by FENE bond.

Phantom Chain

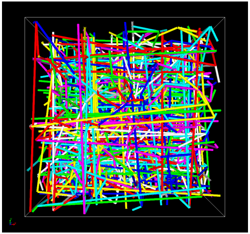


KG Chain



Analysis of Entanglements in Network: Z1-code

[c]



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

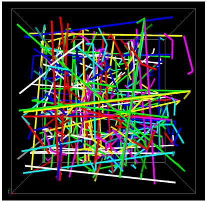
Z1-code?

- Z1-code is an algorism to visualize and count entanglements[a]

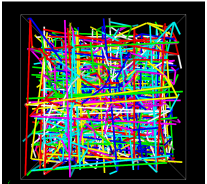
[a] M. Kröger, Comput. Phys. Commun. 168, 209 (2005)

Reduced Entanglements by NPT Model

- 4-Chain-NPT
  $< Z >_{Z1} = 0.36$

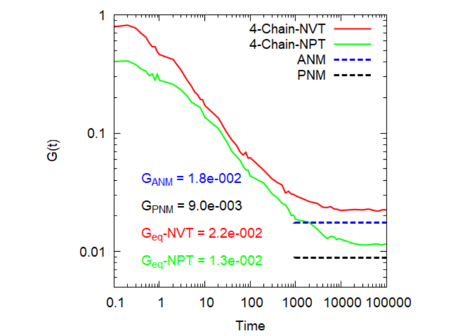


- 4-Chain-NVT
  $< Z >_{Z1} = 1{,}04$



$G(t)$

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



Entanglement effect in Slip-tube Model

Entanglement in Slip-tube Model

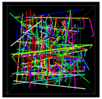
Theoretical model by Rubinstein[a]

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

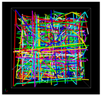
and L is the number of slip-links per network chain

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

NPT
(less Entgld.)



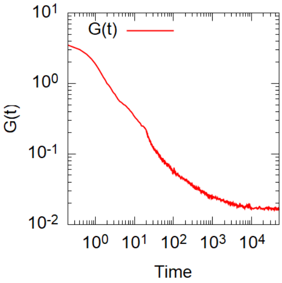
NVT
(well Entgld.)



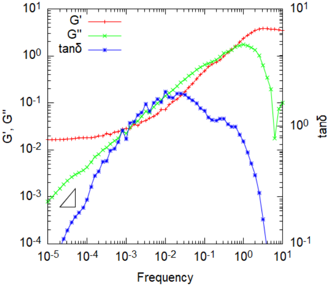
Ensemble	NPT	NVT
Chains, ν	768, 0.018	
$G_c = \nu \times (1 - 2/4)$	0.009	
Entanglements	278	800
Entangled Chains	249	557
L	278/768=0.36	800/768=1.04
$G_e = 4/7 \times \nu \times L$	0.004	0.011
$G_{calcd.} = G_c + G_e$	0.013	0.020
$G_{measd.}$	0.013	0.022

G(t) for Step Shear and Dynamic Rheo-Spectrum

G(t) for Step Stretch



Dynamic Viscoelastics

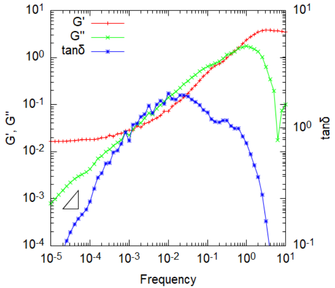


Conditions

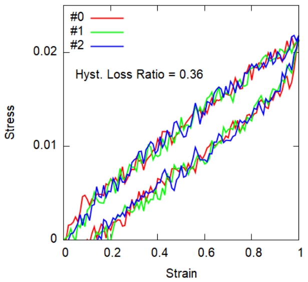
- 4-Chain KG-NW(N=50)
- Step Stretch: $\lambda = 2$
- G(t) is transformed to Dynamic Viscoelastic Spectrum

Mechanical Hysteresis Loss

Dynamic Viscoelastics



Hysteresis by Cyclic Shear

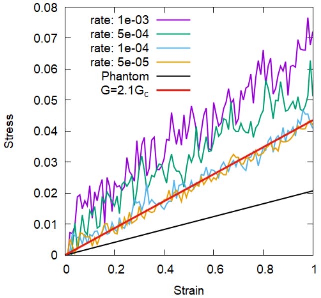


Conditions

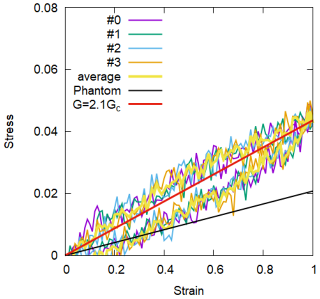
- 4-Chain KG-NW(N=50)
- Cyclic Shear: $\gamma = 1$, $\dot{\gamma} = 5e^{-5}$

4-Cain NW のせん断変形時のヒステリシス

- PNM へと漸近する変形速度 ($\dot{\gamma} = 2e^{-4}$) で複数回の連続した変形に対しても迅速な回復を伴った力学的ヒステリシス (Hysteresis loss $\simeq$ 0.34) を示した。

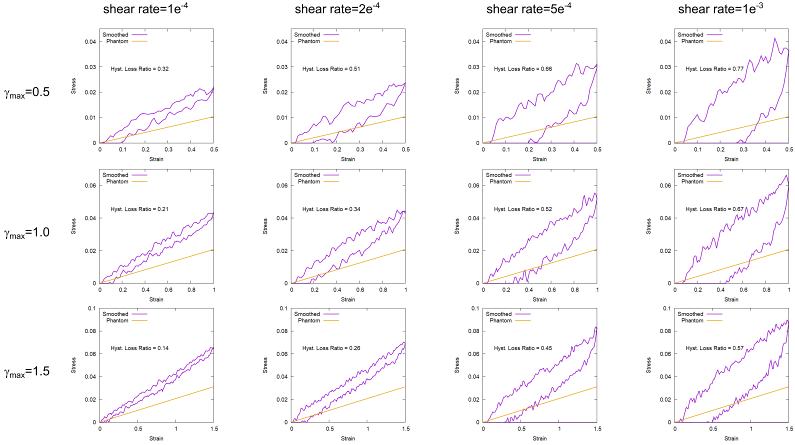


Stress-Strain Curves for 4-chain NW



Hysteresis Response with Cyclic Deformations

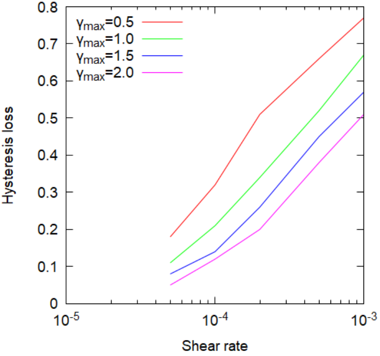
各種の変形条件での力学的ヒステリシス



Hysteresis losses for valid shear rate and maximum deformation

ヒステリシスロス

- 変形速度の低下に伴いヒステリシスロスは減少
- $\dot{\gamma} \sim 1e^{-5}$ 程度のオーダーの時間スケールで消失



Comparison of Hysteresis losses for 4-Chain NW

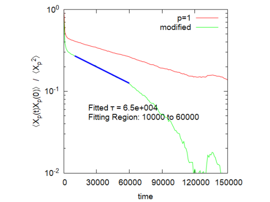
ストランドの最長緩和時間

最長緩和時間 (τ) を評価

- ストランドのラウスモード（p=1）の自己相関関数 $C_p(t)$

$$C_p(t) = \langle X_p(t) X_p(0) \rangle / \langle X_p^2 \rangle$$

- 相関関数の振る舞い
  - 長時間極限で一定値に収束
  - 空間的な拘束のため
  - $C_p(\infty)$ を差し引いて評価



$C_{p1}(t)$ for equilibrated structure

$$\tau \simeq 6.5e^4$$

ヒステリシスロスが消失する変形速度 ($\sim 1e^{-5}$) と対応

Conclutions

- Introducing random connectivity, MD simulation studies were carried out.
- To investigate the criteria for Phantom Network Model, Two model chains are used.
  - Employing phantom chain, basics for PNM is examined.
    - Proper strand length is the key for PNM.
    - Functionality effect was confirmed.
  - Changing the chain to KG Chain, constraints effects are investigated.
    - Trapped Entanglement was explained by Slip-tube Model
    - Hysteresis