Relaxation Behavior of Network Polymers with Random Connectivity

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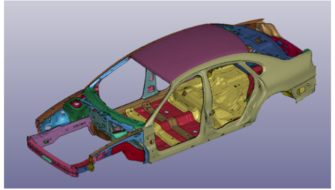
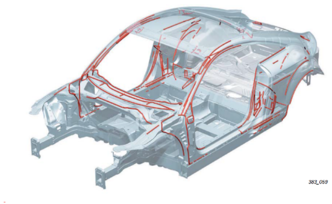
1. Introduction
   - Adhesive Bonding Technology as a Key to Multi-Materialization
   - Theoretical Models for Rubber
   - Objectives
2. Simulation
   - Generation Recipe of Random Networks
   - Phantom and KG Chains as Strands
   - Simulation Conditions
3. Results
   - Networks with Phantom Chains
   - KG Chain Networks
   - Relaxation in KG Networks

Adhesive Bonding Technology





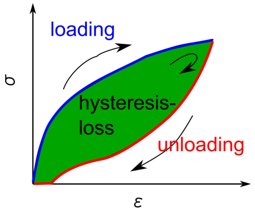
- For Energy conservation
  - weight reduction of cars
  - multi-materialization
  - adhesive bonding technology is a key
- durability in long-term use is important
  - Especially for fatigue tests
  - reliability of polymer materials is still ambiguous

Let me start with this slide as background.

1. focusing on Energy conservation
   - weight reduction of cars is a big issue.
   - for that purpose, multi-materialization, using Aluminum, Magnesium, CFR(T)Ps is discussed.
   - (POINT) these different colors
   - in the process, adhesive bonding technology is a big key.
   - these red lines are the adhesive bonded.
2. requirements for network polymers used as adhesives are
   - not only high primary mechanical properties
   - but also the ability to withstand fatigue tests

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



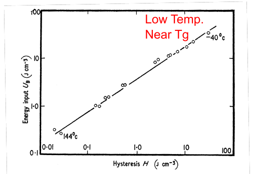


FIG. 1.—Energy input at break U_B against hysteresis H at break for SBR gum vulcanizate over a temperature range of −40 to 144° C.

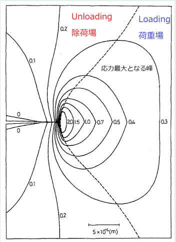
[a] K.A.Grosch, J.A.C.Harwood, A.R.Payne, Rub. Chem. Tech., 41, 1157(1968)
[b] A.R.Payne, J.Poly.Sci.:Sympo., 48, 169(1974)

- hyst
  - Mechanical Hysteresis is illustrated in this figure(POINT).
  - this green area is equivalent to Energy dissipation during cycle
  - Positive correlation with fracture energy had been reported by Payne.
- The origin of hysteresis loss is also categorized by Payne
  - We focuse on this Viscoelasticity based one

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)

- 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
- Bigger Hysteresis Loss results in Higher Toughness.

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)

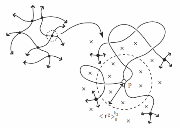
Here, the classical theories of rubber Elasticity are summerized.

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

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
  - 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

- In the vicinity of Junction Point
  - Junction points are surrounded by many of adjacent strands.
  - Because of other strands, Fluctuation of junctions are suppressed.
- Effect is mainly two.
  - One is Suppress the fluctuation of Junction Point
    - Affect G_c, and Deviate from Phantom Network Model
  - Other is Strands Entangles each other
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    - Generate additional G_e
- Concerning these effect, two approach was proposed
  - One is Constrained Junction model, on the uniaxial deformation, constraints are released and G approaches to G_c
  - Other is Considering topological effect, those were counted as Ge

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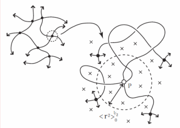
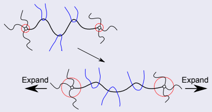


Effect of other strands (Combination of G_c and G_e)

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

$$G_e = T_e G_N^0$$



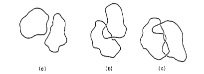


Figure 4. Three topological relationships between two closed loops: (a) not entwined, (b) once entwined, (c) twice entwined.

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

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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]

[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)

- These three models are the major recent approach for a evaluation of constraints.
- All recent models are based on Phantom Network Model.
- The latest Rubinstein's Slip-tube model" seems proper(POINT).
- In that model, Gc and Ge is separated simply.

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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

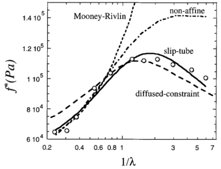

Figure 5. Fit of the data by Pak and Flory[20] on cross-linked poly(dimethylsiloxane) (open circles) by the diffused-constrained model (dashed line), Mooney−Rivlin expression (dotted line), nonaffine tube model (dash−dotted line), and the slip-tube model (solid line).

[a] A. Kloczkowski, J.E. Mark, B. Erman, Macromol., 28, 5089 (1995)

[b] M. Rubinstein, S. Panyukov, Macromol., 30, 25, 8036 (1997)

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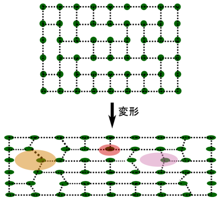
Random Networks as a key for PNM

- 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)

- Introduction of Random Connectivity is known to a key for Phantom Network model.
- As a result, Criteria for PNM is fulfilled
- these two previous works deal random network
- the network is not so simple discussion is complicated.

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.
     - KG Chain:
     - Excluded Volume Effect
     - No mutual crossing of Strands

This is an objective of this work.

- 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.
     - KG Chain:
     - Excluded Volume Effect
     - No mutual crossing of Strands
     - Phantom chain has nothing, just connection.

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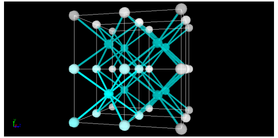
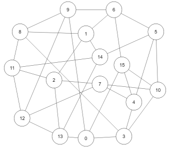
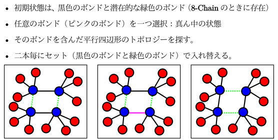
- Relaxation in KG Networks

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.







- 8-Chain Model is used as starting structure in Real space.
  - Randomly selected edge is removed until desired functionality.
  - Topological model is generated.
- Randomness is introduced in topological space, by edge exchange, random connectivity is introduced for each node.
- Corresponding real space structure is generated.
- According to e2e distance of strand, system size and multiplicity are varied to keep $\rho = 0.85$.

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.

- Conditions for Phantom and KG Chains are shown here.
- Important point is,
- Employing "Force Cap LJ" for 1, 3 interaction of inner chain segments,
- e2e length of KG Chains is emulated in phantom chain.

Reluxation of Initial Structure in KG Network

KG Network: KG chain as strand

- Relaxation of initial structure is important.

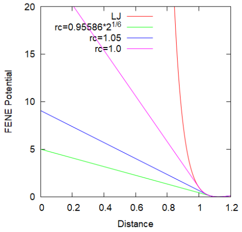
$$U_{KG}(r) = \begin{cases} U_{nonbond} = U_{LJ} \text{ where } r_c = 2^{(1/6)}\sigma \\ U_{bond} = U_{LJ} + U_{FENE} \end{cases}$$

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

- For KG model without mutual chain crossing,
- Relaxation of initial structure is important.

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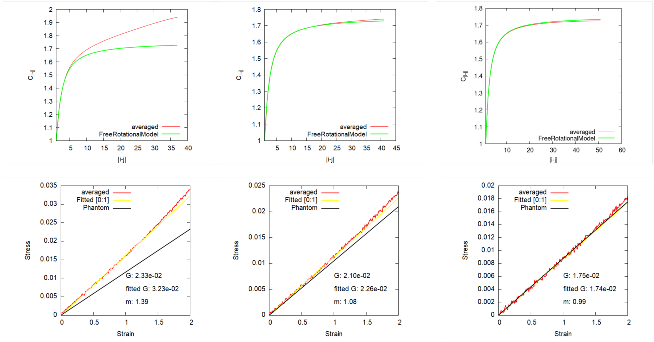
Strand length Effect for Phantom Chain NW(f=4)

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

N = 36
Shrinkage = 1.0

N = 40
Shrinkage = 0.89

N = 48
Shrinkage = 0.85



- Keeping the density, Starand length were varied.
- Shorter chain length resulted in higher modulus.
- WIth proper chain length, N-48, PNM nature is found.
- These results were explained by reduced fluctuation mobility of junction point

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

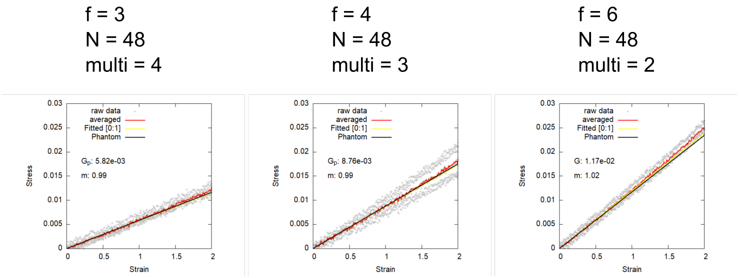


Figure: Comparison of Functionality (f = 3, 4, 6)

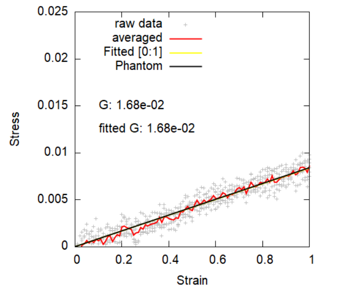
- WIth proper chain length, N-48, PNM nature is found.
- functionality effect on modulus is perfect.

Mechanical Responce for KG Chains

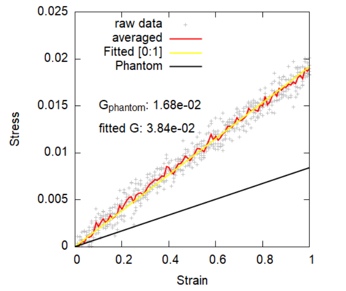
4-Chain Random Network with KG Chain

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

Phantom Chain

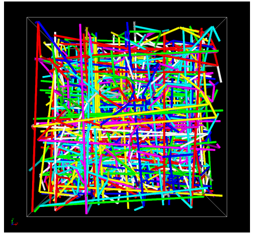


KG Chain



- For KG NW, Modulus is much higher than PNM Predict.

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?

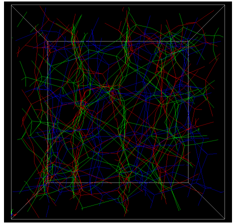
- Z1-code is an algorism to visualize and count entanglements[a]

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

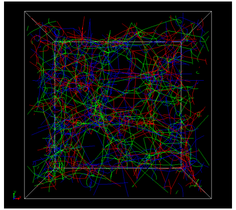
- to investigate for higher modulus,
- Employing Z1-code, number of entanglements per chain Z was calculated.
- the number is almost the same as homo-polymer melts.

Reduced Entanglements by NPT Model

- 4-Chain-NPT

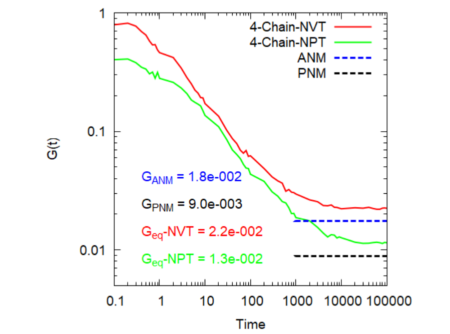


- 4-Chain-NVT



$G(t)$

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



- Employing NPT relaxation, number of entanglements are reduced.
- equilibrated modulus on stress relaxation is much reduced.

Entanglement effect in Slip-tube Model

Entanglement in Slip-tube Model

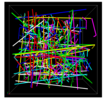
Theoretical model by Rubinstein[a]

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

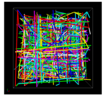
and L is the number of slip-links per network chain

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

NPT
(less Entgld.)



NVT
(well Entgld.)

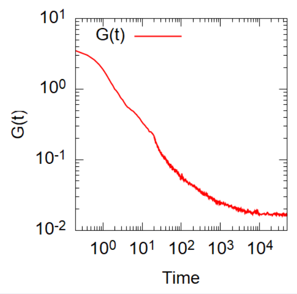


Ensemble	NPT	NVT
Chains, ν	768, 0.018	
$G_c = \nu \times (1 - 2/4)$	0.009	
Entanglements	278	800
Entangled Chains	249	557
L	278/768=0.36	800/768=1.04
$G_e = 4/7 \times \nu \times L$	0.004	0.011
$G_{calcd.} = G_c + G_e$	0.013	0.020
$G_{measd.}$	0.013	0.022

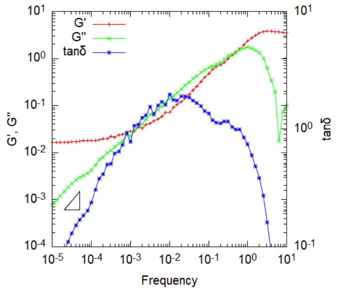
- Adapting Slip-tube model estimation, the measured modulus is fully explained.

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

G(t) for Step Stretch



Dynamic Viscoelastics



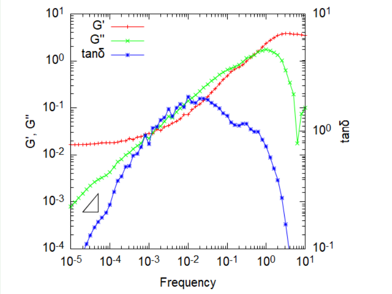
Conditions

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

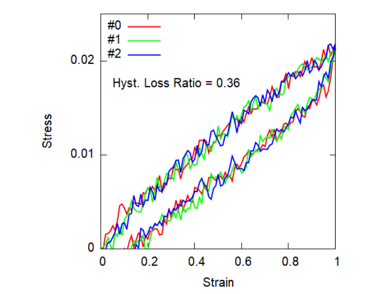
- The $\tan\delta$ of the glass transition decayed on a time scale of this region(POINT)
- it was longer than the longest relaxation time of homo-polymers of comparable length.
- This prolonged relaxation time can be attributed to the reduced mobility of the cross-linking points due to the network structure

Mechanical Hysteresis Loss

Dynamic Viscoelastics



Hysteresis by Cyclic Shear



Conditions

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

- Around this region(POINT), Hysteresis loss was found.
- Network connectivity should affect the nature of hysteresis loss.

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

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