

Relaxation Behavior of Network Polymers with Random Connectivity

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July 19, 2023

1 Introduction

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

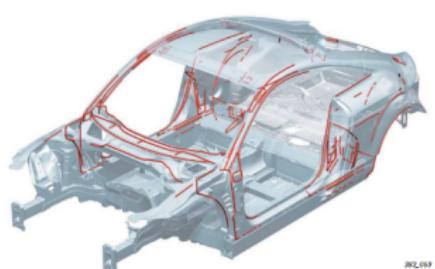
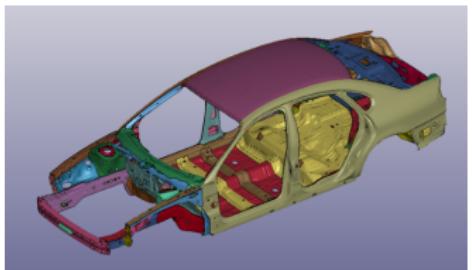
2 Simulation

- 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

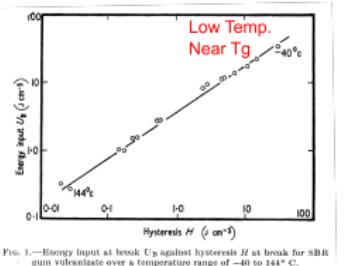
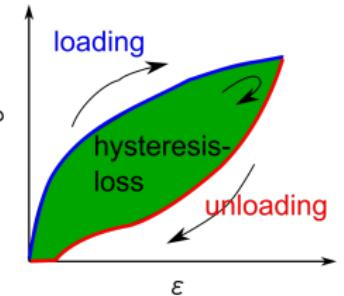


Fig. 1.—Energy input at break U_b against hysteresis H at break for SBR gum vulcanizate over a temperature range of -40 to 144°C .

^aK.A.Grosch, J.A.C.Harwood, A.R.Payne,
Rub. Chem. Tech., 41, 1157(1968)

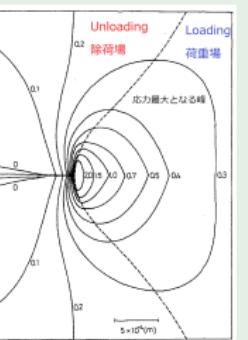
^bA.R.Payne, J.Poly.Sci.:Sympo., 48, 169(1974)

- 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 focus 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 \Rightarrow Energy Dissipation
 - The progress of Crack is Suppressed
- Bigger Hysteresis Loss results in Higher Toughness.



^aE.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 Points fluctuation

Affine Network Model ^a

$$G_{affine} = \nu k_B T$$

ν : Number density of strands in the system

Phantom Network Model ^a

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

f : Functionality of Junction Points

^aP.J. Flory, Principles of Polymer Chemistry, (1953)

^aH.M. James, E.J. Guth, Chem. Phys., 21, 6, 1039 (1953)

Here, the classical theories of rubber Elasticity are summarized.

- 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
 - Works as a Junction Point
 - 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 G_e

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- Fluctuation of junctions are suppressed.



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

$$G_e = T_e G_N^0$$

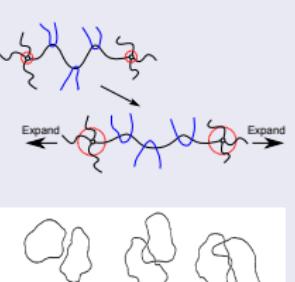


Figure 4. Three topological relationships between two closed loops.
(a) not entwined, (b) once entwined, (c) twice entwined.

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^aP.J.Flory, J.Chem.Phys., 66, 12, 5720 (1977)

^bD.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

- These three models are the major recent approach for a evaluation of constraints.
- The latest Rubinstein's Slip-tube model" seems proper(POINT).
- All recent models are based on Phantom Network Model.

^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

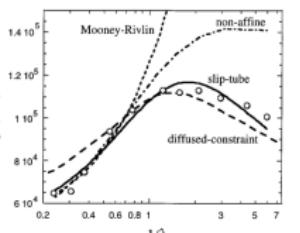


Figure 5. Fit of the data by Pak and Flory²⁰ on cross-linked poly(dimethylsiloxane) (open circles) by the diffused-constrained model (dashed line), Mooney-Rivlin expression (dotted line), nonaffine tube model (dash-dotted line), and the slip-tube model (solid line).

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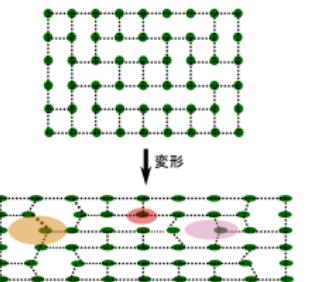
^aA. Kloczkowski, J.E. Mark, B. Erman, *Macromol.*, 28, 5089 (1995)

^bM. 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{r} of strands are **fluctuate**
 - fluctuations $\Delta r = r - \bar{r}$ 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



^aP. J. Flory, Proc. R. Soc. London. A, 351, 351 (1976)

^bG.S. Grest, et.al., Non-Cryst. Solids, 274, 139 (2000)

^cY. 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
- in these previous works, the network is not so simple.

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.

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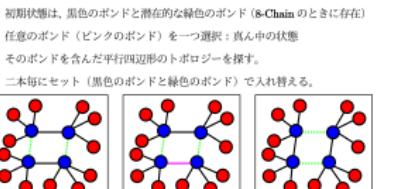
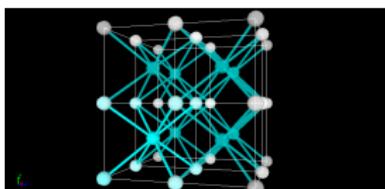
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- Relaxation in KG Networks

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.



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- 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

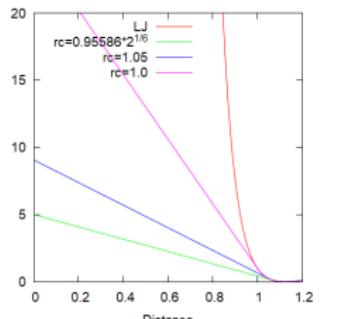
- Relaxation of initial structure is important.

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

Initial Structure Relaxation

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

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



- force-capped-LJ Pot.
- gradually entangled

^aR. Auhl et al. J. of Chem. Phys., 119, 12718 (2003)

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

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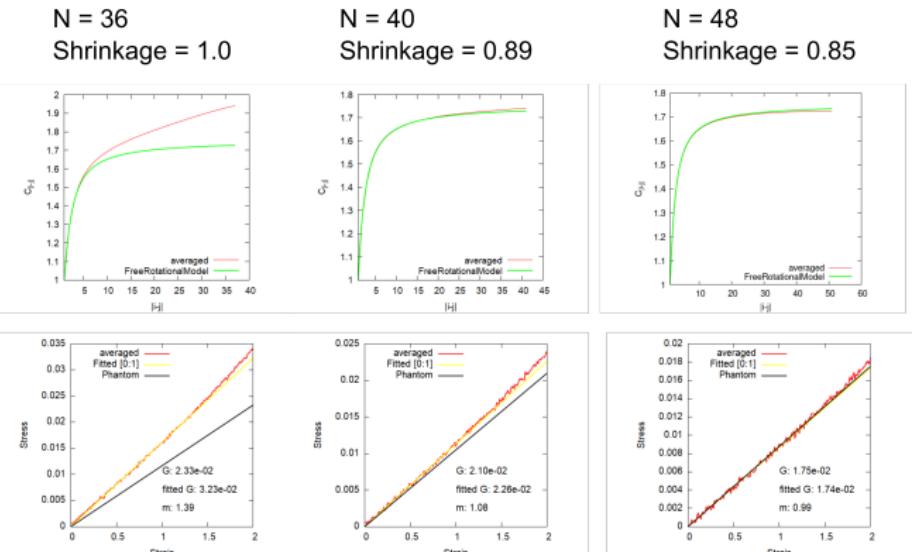
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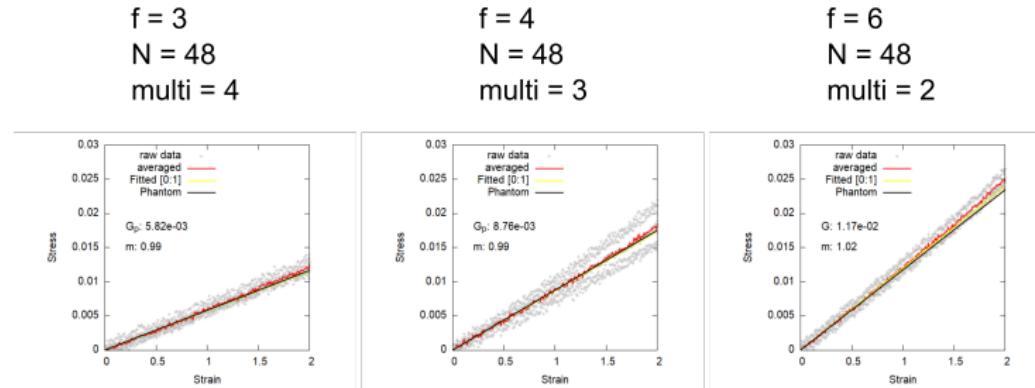
Strand length Effect for Phantom Chain NW($f=4$)

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



- 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 ($f = 3, 4, 6$)



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

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

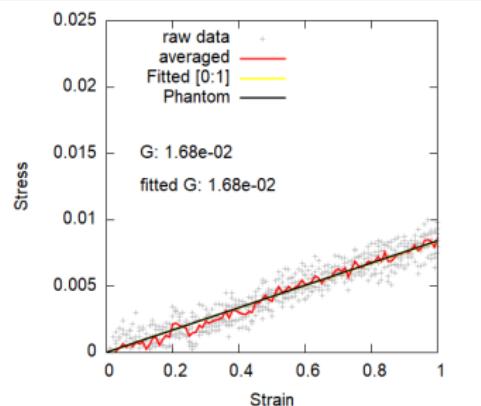
- For KG NW, Modulus is much higher than PNM Predict.

Mechanical Response for KG Chains

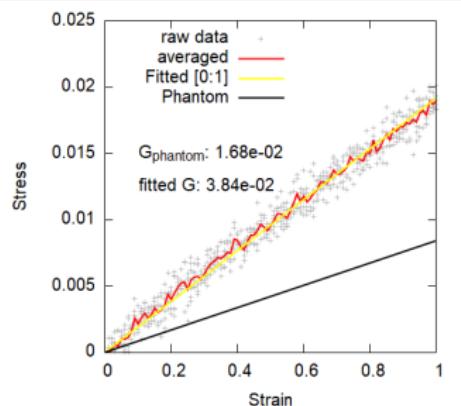
4-Chain Random Network with KG Chain

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

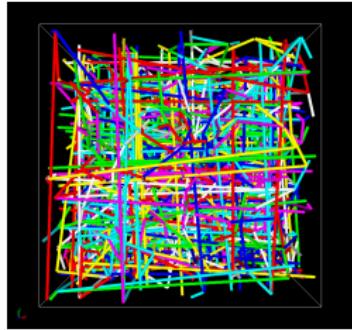
Phantom Chain



KG Chain



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
$\langle Z \rangle_{z1}$	1.02	1.04

Z1-code?

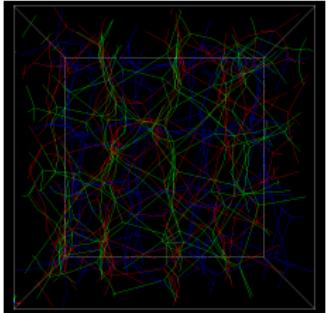
- Z1-code is an algorithm to visualize and count entanglements^a

^aM. Kröger, Comput. Phys. Commun. 168, 209 (2005)

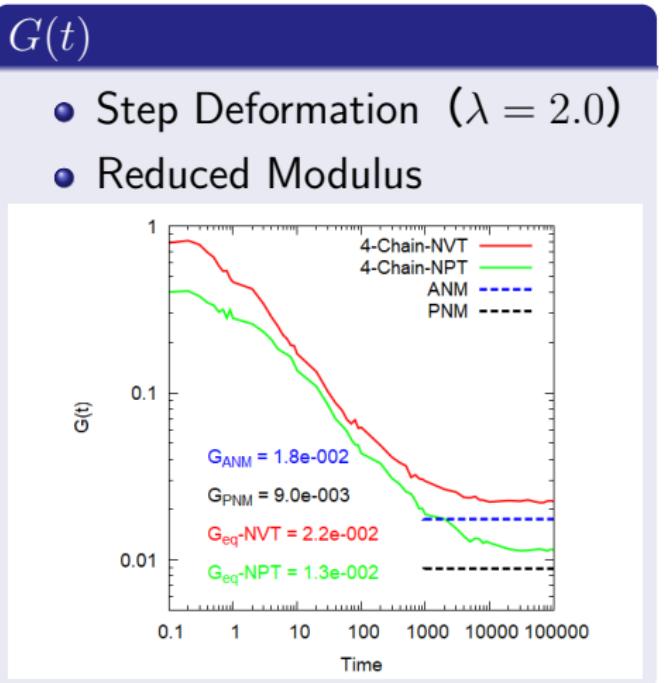
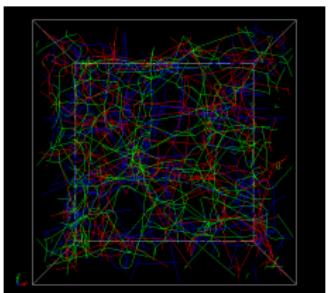
- to investigate for higher modulus,
- Employing Z1-code, number of entanglements per chain Z was calculated.
- the number is almost the same as homo-polymer melts.

Reduced Entanglements by NPT Model

- 4-Chain-NPT



- 4-Chain-NVT



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

Entanglement effect in Slip-tube Model

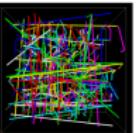
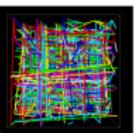
Entanglement in Slip-tube Model

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

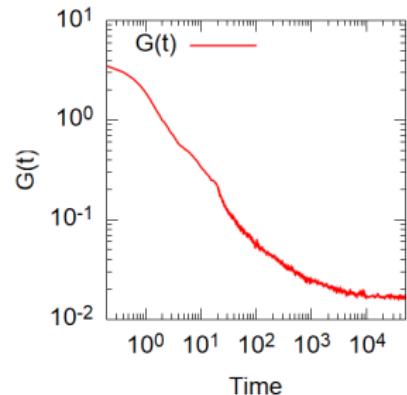
^aM. Rubinstein, S. Panyukov, Macromolecules, 35, 6670 (2002)

	Ensemble	NPT	NVT
	<i>Chains, ν</i>	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

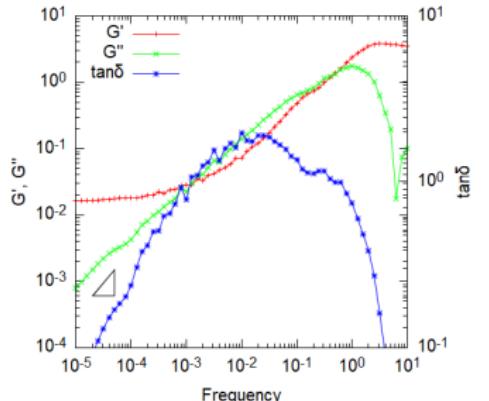
- Adapting Slip-tube model estimation, the measured modulus is fully explained.

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

G(t) for Step Stretch



Dynamic Viscoelastics



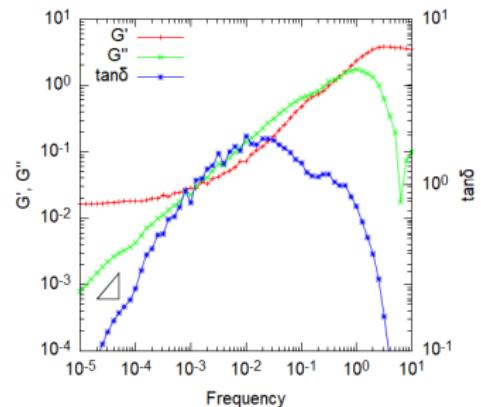
Conditions

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

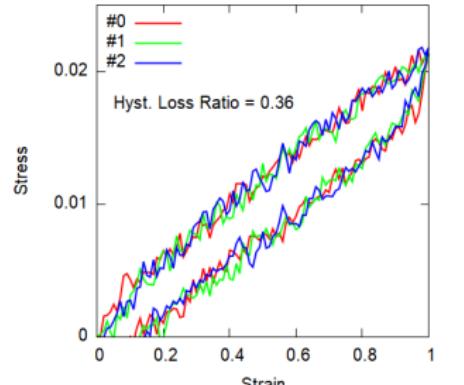
- The $\tan\delta$ of the glass transition decayed on a time scale of this region(POINT)
- it was longer than the longest relaxation time of homo-polymers of comparable length.
- This prolonged relaxation time can be attributed to the reduced mobility of the cross-linking points due to the network structure

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.

Conclusions

- 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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