

# 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

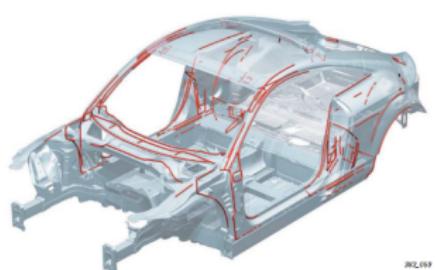
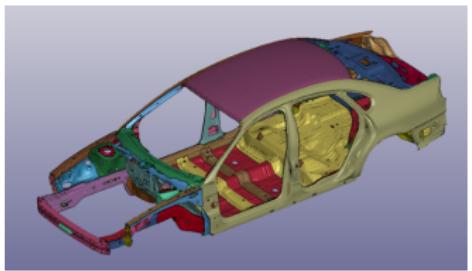
## 2 Simulation

- 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<sup>a</sup>
- The origin of Hysteresis Loss<sup>b</sup>
  - Viscoelastics
  - Crystallization
  - Derived by added filler

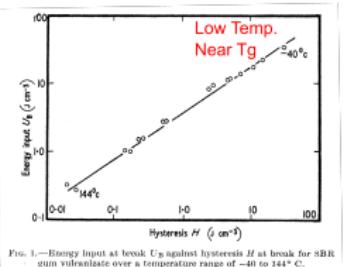
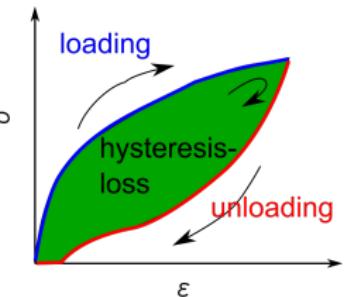


Fig. 1.—Energy input at break  $U_b$  against hysteresis  $H$  at break for SBR gum vulcanizate over a temperature range of  $-40$  to  $144^\circ\text{C}$ .

<sup>a</sup>K.A.Grosch, J.A.C.Harwood, A.R.Payne,  
Rub. Chem. Tech., 41, 1157(1968)

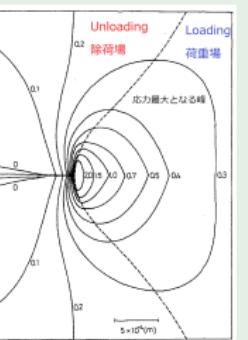
<sup>b</sup>A.R.Payne, J.Poly.Sci.:Sympo., 48, 169(1974)

- 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 focus on this Viscoelasticity based one

# Andrews Theory for Rubber Toughness

## Andrews Theory

- Focused on stress field around the crack<sup>a</sup>
  - 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.



<sup>a</sup>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 Points fluctuation

### Affine Network Model <sup>a</sup>

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

$\nu$ : Number density of strands in the system

### Phantom Network Model <sup>a</sup>

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

$f$ : Functionality of Junction Points

<sup>a</sup>P.J. Flory, Principles of Polymer Chemistry, (1953)

<sup>a</sup>H.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  $G_e$
- Previous models
  - On the uniaxial deformation, constraints are released and  $G$  approaches to  $G_c$
  - Considering topological effect can be counted as  $G_e$

# Constraint Factors for Junction Points and Strands

## Vicinity of Junction Point

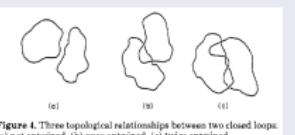
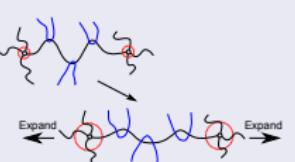
- Junction points are surrounded by many of adjacent strands(x in fig.).
- Fluctuation of junctions are suppressed.



## Effect of other strands (Combination of $G_c$ and $G_e$ )

- Constrained Junction Model
  - $G$  approaches to  $G_c$ .<sup>a</sup>
- Topological relationships
  - Contribution of entanglement.<sup>b</sup>

$$G_e = T_e G_N^0$$



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  - Junction points are surrounded by many of adjacent strands.
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  - Considering topological effect can be counted as  $G_e$

<sup>a</sup>P.J.Flory, J.Chem.Phys., 66, 12, 5720 (1977)

<sup>b</sup>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.<sup>a</sup>
- Nonaffine Tube Model
  - Improved model of "Edwards' Tube Model".<sup>b</sup>
- Slip-tube Model
  - A pairwise interaction of chains is introduced.<sup>c</sup>

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

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<sup>a</sup>A. Kloczkowski, J.E. Mark, B. Erman, *Macromol.*, 28, 5089 (1995)

<sup>b</sup>M. Rubinstein, S. Panyukov, *Macromol.*, 30, 25, 8036 (1997)

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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  $\nu$  is the number density of network chains,  
 $L$  is the number of slip-links per network chain

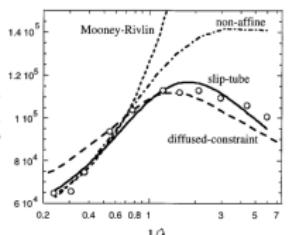


Figure 5. Fit of the data by Pak and Flory<sup>20</sup> on cross-linked polydimethylsiloxane (open circles) by the diffused-constrained model (dashed line), Mooney-Rivlin expression (dotted line), nonaffine tube model (dash-dotted line), and the slip-tube model (solid line).

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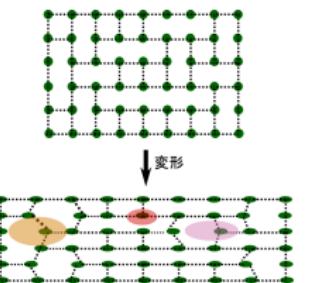
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# Random Networks as a key for PNM

- Introduction of **Random Connectivity**.
- **Criteria for PNM** is fulfilled<sup>a</sup>.
  - 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<sup>b</sup>
  - Primitive Chain Network Simulation<sup>c</sup>



- Introduction of Random Connectivity is known to a key for PNM
- As a result, Criteria for PNM is fulfilled
- in these previous works, the network is not simple.

<sup>a</sup>P. J. Flory, Proc. R. Soc. London. A, 351, 351 (1976)

<sup>b</sup>G.S. Grest, et.al., Non-Cryst. Solids, 274, 139 (2000)

<sup>c</sup>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.
    - KG Chain:
    - Excluded Volume Effect
    - No mutual crossing of Strands

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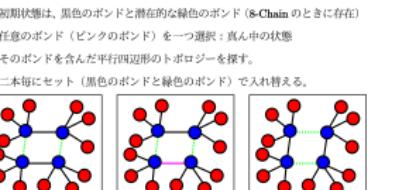
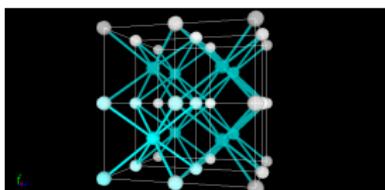
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- Simulation Conditions

## 3 Results

- Networks with Phantom Chains
- KG Chain Networks
- 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.



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 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

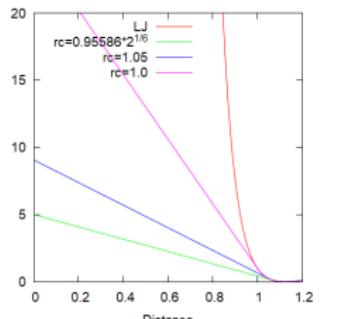
- Relaxation of initial structure is important.

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

## Initial Structure Relaxation

- According method of Auhl<sup>a</sup>
  - 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

<sup>a</sup>R. 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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## 2 Simulation

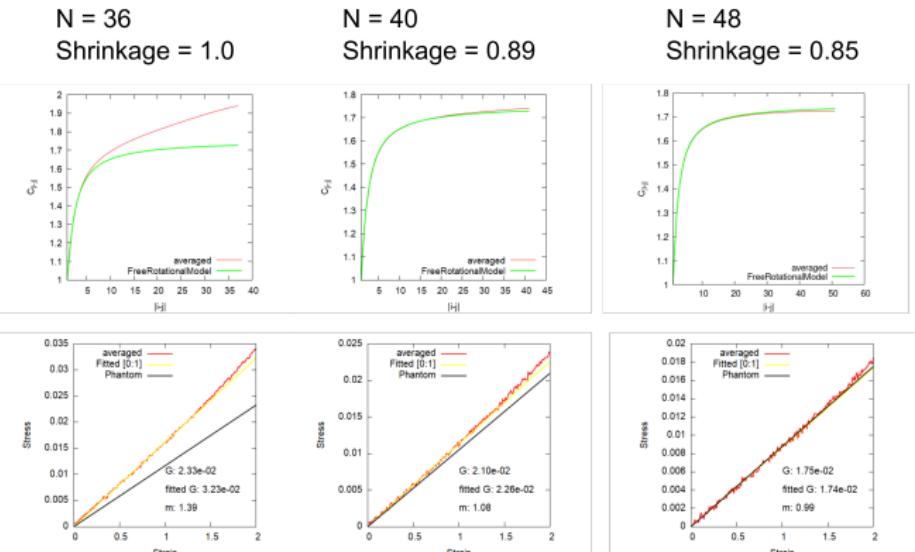
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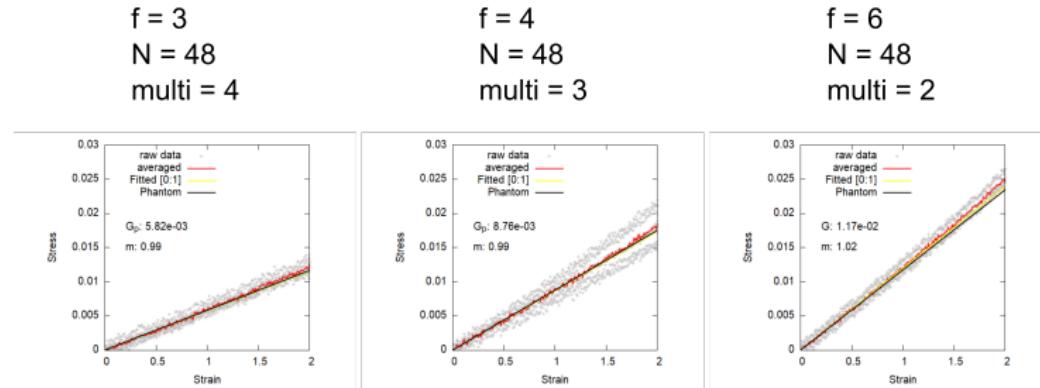
# Strand length Effect for Phantom Chain NW(f=4)

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

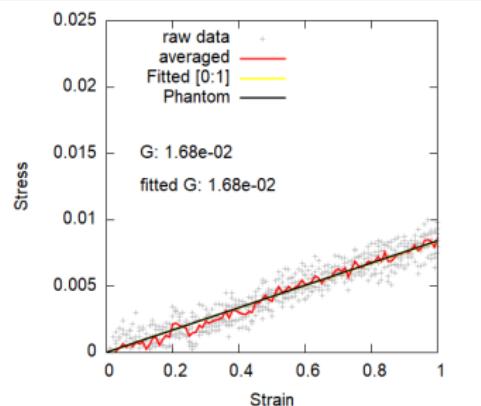
- For KG NW, Modulus is much higher than PNM Predict.

# Mechanical Response for KG Chains

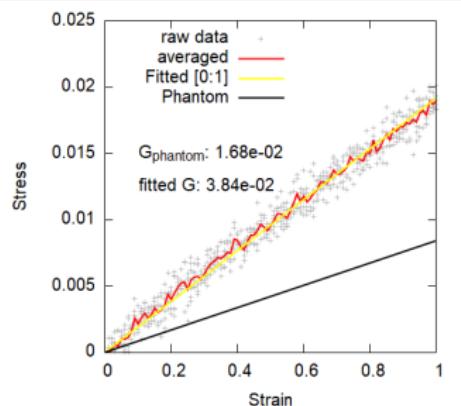
## 4-Chain Random Network with KG Chain

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

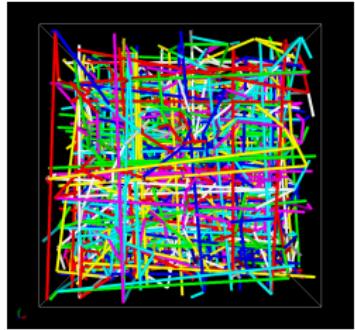
Phantom Chain



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?

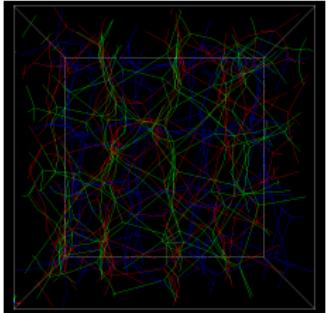
- Z1-code is an algorithm to visualize and count entanglements<sup>a</sup>

<sup>a</sup>M. Kröger, Comput. Phys. Commun. 168, 209 (2005)

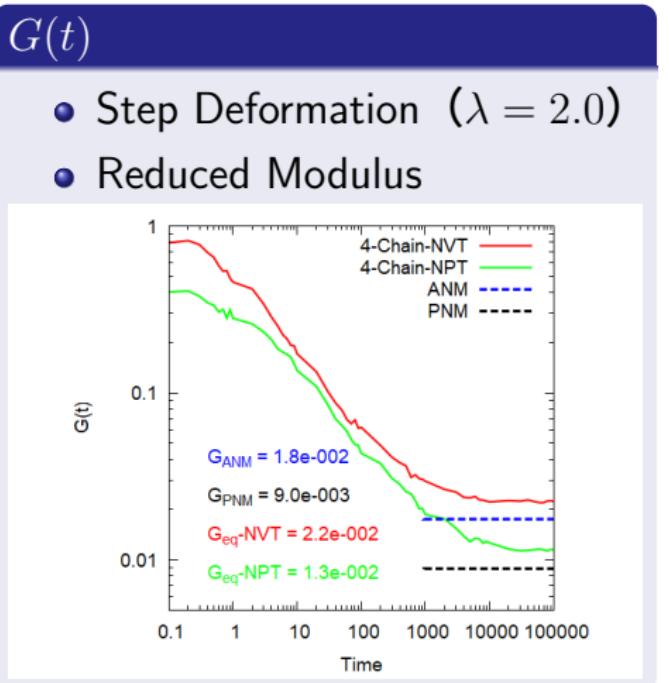
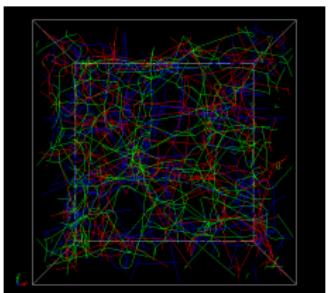
- to investigate for higher modulus,
- Employing Z1-code, number of entanglements per chain Z was calculated.
- the number is almost the same as homo-polymer melts.

# Reduced Entanglements by NPT Model

- 4-Chain-NPT



- 4-Chain-NVT



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

# Entanglement effect in Slip-tube Model

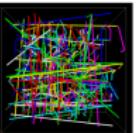
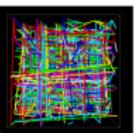
## Entanglement in Slip-tube Model

Theoretical model by Rubinstein<sup>a</sup>

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

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

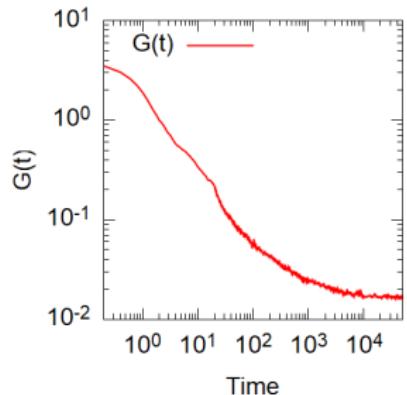
<sup>a</sup>M. Rubinstein, S. Panyukov, Macromolecules, 35, 6670 (2002)

	Ensemble	NPT	NVT
	<i>Chains, <math>\nu</math></i>	<b>768, 0.018</b>	
	$G_c = \nu \times (1 - 2/4)$	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
	$G_{calcd.} = G_c + G_e$	<b>0.013</b>	<b>0.020</b>
	$G_{measd.}$	<b>0.013</b>	<b>0.022</b>

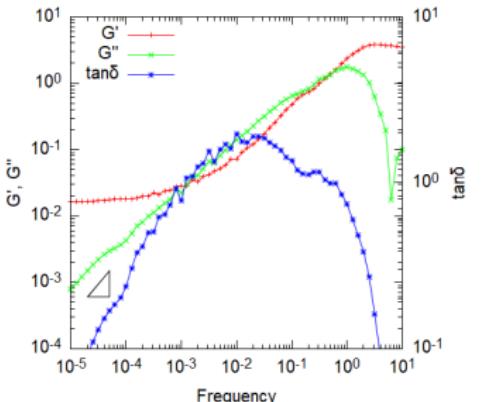
- Adapting Slip-tube model estimation, the measured modulus is fully explained.

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

## G(t) for Step Stretch



## Dynamic Viscoelastics



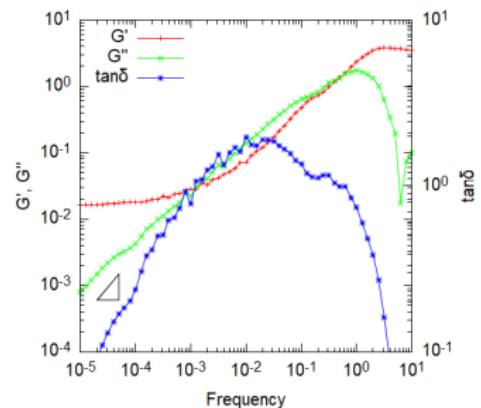
## Conditions

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

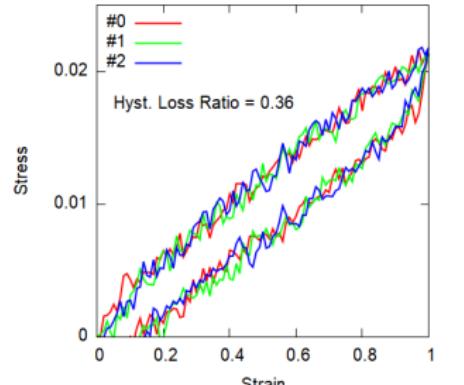
- The  $\tan \delta$  of the glass transition decayed on a time scale of this region(POINT)
- it was longer than the longest relaxation time of homo-polymers of comparable length.
- This prolonged relaxation time can be attributed to the reduced mobility of the cross-linking points due to the network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