

Relaxation Behavior of Network Polymers with Random Connectivity

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Introduction

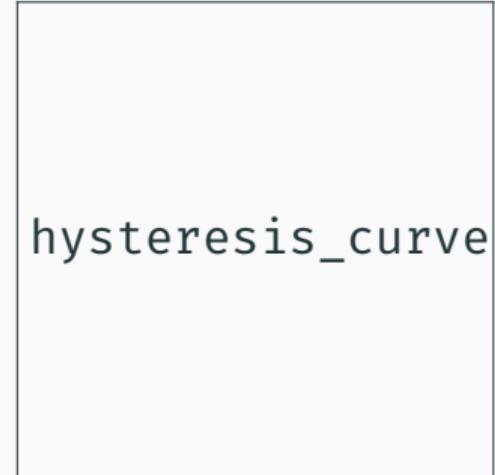
Adhesive Bonding Technology

adhesive_car2.png

- 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

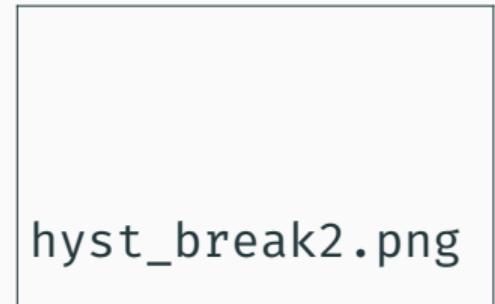
- Mechanical Hysteresis Loss
 - Reduced stress on unloading
 - Energy dissipation during cycle
 - Positive correlation with fracture energy^a
- The origin of Hysteresis Loss^b
 - Viscoelastics
 - Crystallization
 - Derived by added filler



hysteresis_curve.png

^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_break2.png

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)

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)

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 C is combination of G_c and G_e

Constraint Factors for Junction Points and Strands

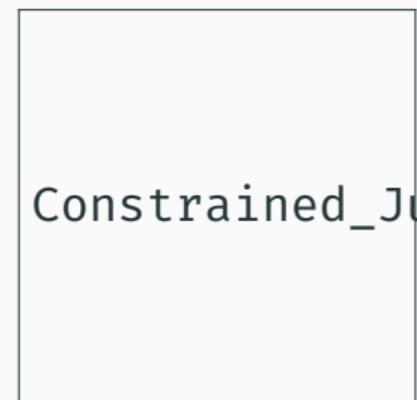
Vicinity of Junction Point

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



Recent approach for Constraints (Entanglements)

- Diffused-Constraint Model
 - Confining potential affect all points along the chain.¹
- Nonaffine Tube Model
 - Improved model of "Edwards' Tube Model".²
- Slip-tube Model
 - A pairwise interaction of chains is introduced.³

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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



random_NW.png

^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)

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