National Journal of Multidisciplinary Research and Development
ISSN: 2455-9040
Impact Factor: RJIF 5.22
www.nationaljournals.com
Volume 3; Issue 1; January2018; Page No. 1359-1361

Various theories of phantom network: A perspective

Mandeep
University of Delhi, Delhi, India

Abstract
The modern concept of polymers is similar as covalently bonded macromolecular structures. The theory of phantom networks was developed in the forties by James and Goth. The network is composed of cross-linked Gaussian chains. It is assumed that there are two types' network junctions. There are various theories of phantom networks. The more detailed analysis of the phantom network is given by the following theories; James and Guth theory, affine models of rubber elasticity of Wall and Flory and Edwards's replica and tube theories.

Keywords: polymer, phantom network, rubber elasticity

Introduction

A polymer is a high molecular weight compound formed by joining a large number of small monomeric units. This process of linking together is called polymerisation. In other words, we can say that a monomer is a small repetitive unit that links together to form a polymer. Polymers are classified in various types on different bases such as on basis of occurrence, basis of structure, on type of monomers etc. Natural polymers and synthetic polymers are the main two types on basis of their occurrence. As the name indicate the natural polymers are those with obtain from natural monomer like Cellulose, Starch etc and synthetic polymers made from synthetic monomers like Nylon, Bakelite. It is reported that on basis of structure a polymer is mainly divided into three category; Linear polymer, Branched polymer, Cross-linked polymer, these polymers are linked linearly, linked via branches and linked cross-linked to form a web respectively. Those polymers which are made up by the polymerisation of one type of monomer unit defined as homopolymers and different types of monomers joined in a same polymer chain is called copolymers. It is found that these copolymers are further divided into random, alternating and graft copolymer on basis of arrangement of monomers.

The modern concept of polymers as covalently bonded macromolecular structures was proposed in 1920 by Hermann Staudinger, who spent the next decade finding experimental evidence for this hypothesis. The World War second era clear the development of a strong commercial polymer industry. The limited or restricted supply of natural materials such as silk and rubber demanded the increased production of synthetic substitutes, such as nylon and synthetic rubber etc. The field of polymer science includes researchers in various disciplines including chemistry, physics, bio-physics and engineering etc. Polymer chemistry is concerned with the chemical synthesis and chemical properties of polymers and polymer physics is concerned with the bulk properties of polymer materials and its applications etc.

An elastomer is a polymer with viscoelasticity, generally having low Young's modulus and high failure strain compared with other materials. In elastomers polymers the polymer chains are held together by weak attractive force. These are the rubbery polymer that can be stretched several times their unstretched lengths and which rapidly return to their original dimensions when the applied stress is released. These polymer are amorphous, have low degree of cross-linking and high degree of elasticity. In this paper, the various theories of phantom networks are discussed. The more detailed analysis of the phantom network is given by the following theories; James and Guth theory, affine models of rubber elasticity of Wall and Flory and Edwards's replica and tube theories.

Result and Discussion

James and Guth theory of phantom networks

The theory of phantom networks was developed in the forties by James and Guth. They that the network is composed of crosslinked Gaussian chains. It is assumed that there are two Types network junctions. Junctions which are at the surface of the rubber are fixed and deform affinely with the macroscopic strain, while the junctions inside the network are free to fluctuate around their mean positions. It is assumed that the behaviour of the network is determined only by the connectivity of network chains. James and Guth neglected the effect of the excluded volume of polymer chains. The configurational partition function Z_N of the network is the product of configurational particle functions of network Gaussian chains.

Assumed equation

$$Z_N = C \prod_{i<j} \exp\left[\frac{1}{2}\sum_i \sum_j \gamma_{ij}(\mathbf{R}_i - \mathbf{R}_j)^2\right] \quad (1)$$

Where C is a normalization constant and the matrix elements γij (γ=−γ') are defined as: equation

$$\gamma_{ij} = \left\{ \begin{array}{l} \frac{3}{2\langle r_{ij}^2\rangle_0} \text{ if } i \text{ and } j \text{ are connected by a chain} \\ 0 \text{ if } i \text{ and } j \text{are not connected} \end{array} \right\} \quad (2)$$

This means that all statistical properties of the network depend on the connectivity matrix Γ defined by the above Eq. (2). One can easily calculate fluctuations of junctions in the phantom network model, and correlations between these fluctuations for the ideal infinite network with the topology of the tree (with functionality φ of network junctions). These quantities are related to the matrix elements of the inverse matrix Γ^{-1}. The mean square fluctuations of the end-to-end vector $\langle (\Delta r)^2 \rangle$ of polymer chains depend on the functionality φ of the network and is given by the formula.
Equation

$$\langle (\Delta r)^2 \rangle = \frac{2}{\phi} \langle r^2 \rangle_0 \tag{3}$$

These fluctuations are assumed to be independent of the macroscopic strain. The mean square end-to-end vector of the chain $\langle (rij)^2 \rangle$ between junctions i and j can be written as:
Equation

$$\langle (r_{ij})^2 \rangle = \langle (\overline{r_{ij}})^2 \rangle + \langle (\Delta r_{ij})^2 \rangle \tag{4}$$

where $\langle (\overline{r_{ij}})^2 \rangle$ is the time averaged mean square end-to-end vector, and $\langle (\Delta rij)^2 \rangle$ represents instantaneous fluctuations in the chain vector $\mathbf{r}ij$ from its average value $\overline{\mathbf{r}_{ij}}$. It is also assumed that average vectors transform affinely with the macroscopic deformation of the rubber, i.e.
Equation

$$\langle (\overline{r_{ij}})^2 \rangle = \lambda_x^2 \langle (\overline{x_{ij}})^2 \rangle_0 + \lambda_y^2 \langle (\overline{y_{ij}})^2 \rangle_0 + \lambda_z^2 \langle (\overline{z_{ij}})^2 \rangle_0 = \frac{1}{3} \langle (\overline{r_{ij}})^2 \rangle_0 \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 \right) \tag{5}$$

Because of this the elastic free energy of the phantom network in the formulation by Flory is
Equation

$$\Delta A_{\text{el ph}} = \frac{1}{2} \xi kT \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right) \tag{6}$$

Where ξ is so-called cycle rank and of the perfect tree-like network defined as:
Equation

$$\xi = \left(1 - \frac{2}{\phi} \right) \nu \tag{7}$$

Where φ is the functionality of junctions in the network (the number of chains connected at each junction) and v is the number of chains. Originally, according to the mathematical graph theory, for any (even imperfect) network the cycle rank is given as the number of scissions necessary to reduce the graph to a spanning tree. By comparing Eq. (7) with the Kuhn–Treloar theory, which gives an equation,

$$\Delta A_{\text{el}} = \frac{1}{2} \nu kT \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right)$$

It is found that the main difference in the elastic free energy is due to the $2v/\varphi$ term which is related to the strain independent fluctuations of the network.

Affine models of rubber elasticity of Wall and Flory

The affine theory developed by Wall and by Flory and assumes that junctions of the network transform affinely with macroscopic strain. The expression of the elastic free energy is similar to the equation of the theory of Kuhn. In the case of swelling of the network there is an extra logarithmic term associated with the volume change of the rubber
Equation

$$\Delta A_{\text{el}} = \frac{1}{2} \nu kT \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right) - \frac{2\nu}{\phi} kT \ln \left(\frac{V}{V_0} \right) \tag{8}$$

Where V is the volume of the network, and V_0 is the volume of the network in the reference state in which the network was formed. Here v is the number of chains and φ is the network functionality. The affine model of the rubber elasticity is very important, because it is a fundamental limiting case in the constrained-junction theory of rubber elasticity of Flory.

Edwards's replica and tube theories

A different approach to the rubber elasticity was developed by Deam and Edwards in 1976. The Edwards approach is based on his earlier works on replica theory developed for solid-state physics in application to amorphous systems. The replica method has been introduced by Edwards to perform statistical mechanics averaging for amorphous systems subject to both internal and external constraints. Because the theory leads to complicated mathematics, the details are skipped here. The main advantage of this approach is that crosslinks could be considered in detail, and various approximations can reduce this theory to other classical theories. The affine and phantom networks become also limiting cases of the Edwards and Deam theory of rubber elasticity.

The replica method was used later by Ball, Doi and Edwards to develop the slip-link model of rubber elasticity. They reported the effects of entanglements along the chain contour on the elastic free energy. The slip-link may slide along the chain contour and is equivalent to an additional crosslink in the network. The final expression for the elastic free energy in this model is

$$\Delta A_{\text{el}} = \frac{1}{2} N_c kT \left\{ \sum_{t=x,y,z} \lambda_t^2 + \frac{N_s}{N_c} \sum_{t=x,y,z} \left[\frac{(1+\eta)\lambda_t^2}{1+\eta\lambda_t^2} + \ln \left(1 + \eta \lambda_t^2 \right) \right] \right\}$$

Where N_c and N_s are the number of chemical crosslinks and sliplinks, respectively, and η=0.234. The slip-link model has been later modified by Edwards and Vilgis.

Another model developed by Edwards is the tube model based on the idea of harmonic-like tube constrains in elastomeric networks. According to the tube theory polymer is trapped inside a tube of diameter a and length L, formed by constraints from neighbouring crosslinks and chains. The elastic free energy in the tube model is larger than the free energy in the Kuhn model, because of the additional contribution of entanglements to the elastic modulus.

Conclusion

According to James and Guth theory, there are two types' network junctions. Junctions which are at the surface of the rubber are fixed and deform affinely with the macroscopic strain and junctions inside the network are free to fluctuate around their mean positions. The behaviour of the network is determined only by the connectivity of network chains. Here, the effect of the excluded volume of polymer chains is neglected. The main advantage of Edwards's replica and tube theories approach is that crosslinks could be considered in detail, and various approximations can reduce this theory compare to other classical theories.

References

1. Ciferri CAJ. Hoeve PJ. Flory, J. Am. Chem. Soc. 1961; 83:1015.
2. Allen A, Kirkham MJ, Padget JC. Price, Trans. Faraday Soc. 1971; 67:1278.
3. Flory PG, Ciferri A, Chiang R. J Am. Chem. Soc. 1961; 83:1023.
4. Erman P, Flory J. Macromolecules. 1982; 15:806.
5. Akagi Y, Katashima T, Katsumoto Y, Fujii K, Matsunaga T, Chung U, Shibayama M, Sakai T. Macromolecules. 2011; 44(14):5817-5821.
6. Rubinstein M, Colby RH. Polymer Physics; Oxford University Press: Oxford, U.K, 2003.
7. Landau LD, Lifshitz EM, Kosevich AM, Pitaevskii LP. Theory of elasticity, 3rd English ed.; Pergamon Press: Oxford, U.K., and New York, 1986.