

Degradation of the Mechanical Properties of Composite Vulcanizates Loaded with Paraffin Wax

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ABSTRACT: A composite of Styrene Butadiene Rubber (SBR) and Natural Rubber (NR) loaded with 40 phr of High Abrasion Furnace (HAF) carbon black is loaded with different concentrations of paraffin wax. From the stress-strain curves, Young's modulus was found to decrease with increasing the amount of added paraffin wax. The modified Mooney-Rivlin equation was used to calculate the parameters C_1 and C_2 . A plot between the true tensile stress as a function of $(\lambda^2 - \lambda^{-1})$ was used to calculate two parameters σ_0 and G , and then both the average molecular weight between crosslinks and the number of effective plastic chains per unit volume were also calculated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2265–2270, 2001

Key words: SBR; NR; carbon black; wax

INTRODUCTION

The importance of polymer composites arises largely from the fact that such low density materials can have unusually high elastic moduli and tensile strength.^{1–4} For the most part, the tensile properties have been quite adequately dealt with by utilizing the theory of elasticity. The molecular theory of rubber elasticity developed by Flory and Erman^{5–8} is based on the idea of constraints imposed by entangled network chains on crosslink fluctuations. For developing a quantitative physical bases for the stiffness and the strength of vulcanizate composites, it has been studied by dealing with the elastic behavior.⁹ Analysis of stress-strain data obtained from rubber was based on the formula⁹

$$E = E_o(1 + 2.5C) \quad (1)$$

where E is the Young's modulus of the rubber composite, E_o is the modulus of the matrix, and C is the volume fraction of the filler.

The classical kinetic theory developed by Wall,¹⁰ Flory,¹¹ and James and Guth¹² attributed the high elasticity of a crosslinked rubber to the change of the conformational entropy of the long flexible molecular chains. The theory predicts the relation

$$\sigma = A \nu k T (\lambda^2 - \lambda^{-1}) \quad (2)$$

where σ is the true stress, ν is the number of effective plastic chains per unit volume, k is Boltzmann's constant, T is the absolute temperature, λ is the extension ratio, and A is a prefactor, depending on the considered model.

In the present work the effect of paraffin wax on the elastic behavior of the (SBR-NR) composite loaded with 40 phr of HAF carbon black has been studied using Mooney-Rivlin and Yong-Hua Zang et al.¹³ relations.

EXPERIMENTAL

A master batch of styrene-butadiene rubber (SBR) and natural rubber (NR) with equal ratios

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Table I Mix Formation of 40 HAF/(SBR-NR) Composites Loaded with Paraffin Wax

Ingredient (phr)	S ₀	S ₁	S ₂	S ₃	S ₄
SBR	50	50	50	50	50
NR	50	50	50	50	50
HAF	40	40	40	40	40
Processing oil	10	10	10	10	10
Stearic acid	2	2	2	2	2
MBTS ^a	2	2	2	2	2
PBN ^b	1	1	1	1	1
Zinc oxide	5	5	5	5	5
Sulfur	2	2	2	2	2
Paraffin wax	0	10	20	30	40

^a Dibenzthiazole disulphide.

^b Phenyl- β naphthylamine.

and loaded with 40 phr (parts per hundred parts of rubber by weight) was prepared. Different concentrations of paraffin wax were then added. All

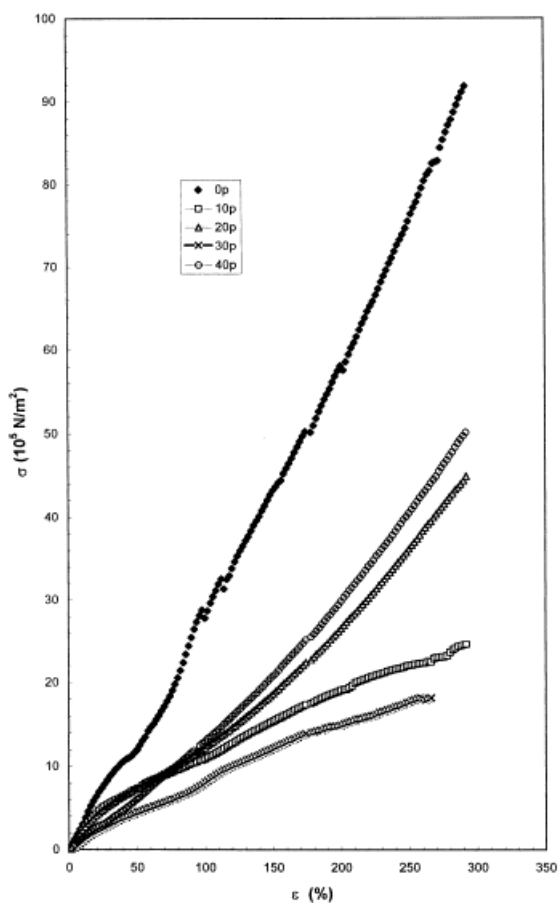


Figure 1 The stress-strain for 40HAF/(SBR + NR) loaded with different concentrations of paraffin wax.

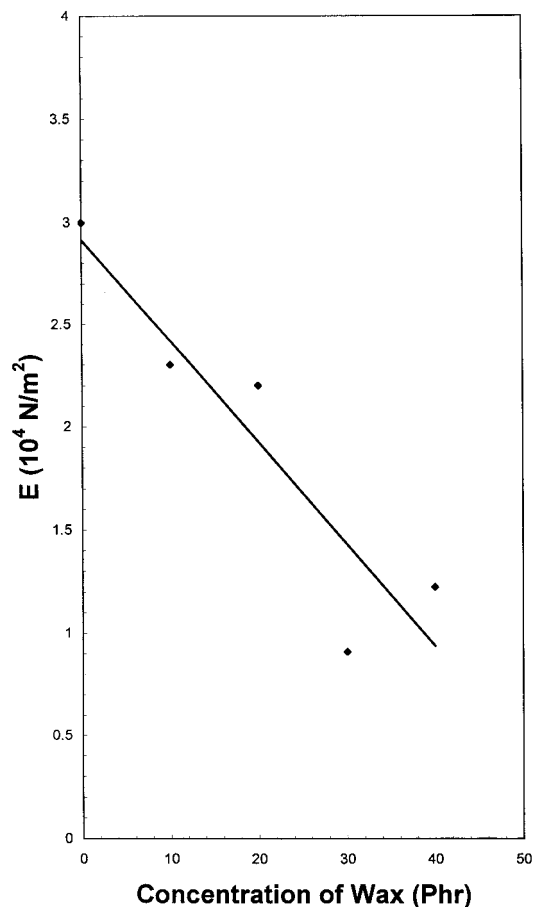


Figure 2 The dependence of Young's modulus on the concentration of paraffin wax for 40HAF/(SBR + NR).

samples were prepared according to the recipes presented in Table I.

All rubber mixtures were prepared on a two roll mill 170 mm in diameter, with a working distance of 300 mm. The speed of the slow roll was 24 revolution per minute and the gear ratio is 1.4. Vulcanization of all samples was conducted at 140°C under a pressure of 40 kg/cm² for 20 min.

The stress-strain measurements were carried out at 30°C using a tensile machine at a constant extension rate of 0.4 mm/s at the Physics Department Suez Canal University.

RESULTS AND DISCUSSIONS

The stress-strain curves of the 40 HAF/(SBR-NR) vulcanizates loaded with different concentrations of paraffin wax are shown in Figure 1. At strains lower than 20%, the kinetic theory holds. At large deformations there is limited extensibil-

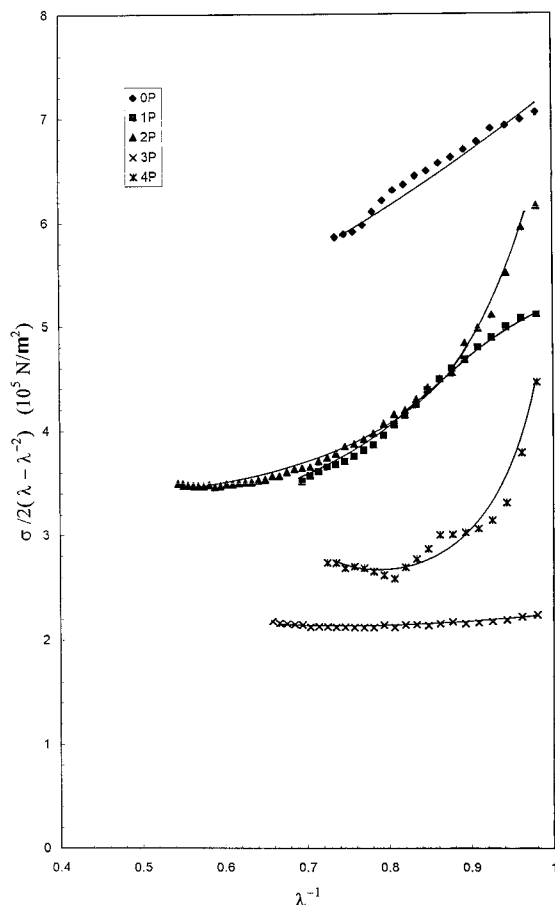


Figure 3 Stress-strain curves in Figure 1 replotted as $\sigma/2(\lambda - \lambda^{-2})$ vs λ^{-1} for studied vulcanizates.

ity of the crosslinked chains. Meanwhile, there is a stress-softening effect at moderate strains. The linear portions (at low extensions) of the curves illustrated in Figure 1 are used to estimate the values of Young's modulus E , which are shown in Figure 2 as a function of the concentration of paraffin wax in phr. The full line in the figure represents the theoretical line given by the equation

$$E = E_o(1 - aC) \quad (3)$$

with $E_o = 2.9 \times 10^4$ N/m² and slope $a = 0.017$. It is clear from the figure that, Young's modulus decreases with the concentration of paraffin wax and indicating the softening properties of waxes and degradation of the matrix.

It has been shown by Rivlin et al.⁹ that the stress-strain behavior of rubber vulcanizates can be described by the Mooney-Rivlin¹⁴ relation which, in simple extension, gives

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} = C_1 + C_2\lambda^{-1} \quad (4)$$

where σ is the true stress, which produces an extension ratio λ in the sample, and C_1 and C_2 are parameters characteristic of the rubber vulcanizate. It has been shown that¹⁵ C_1 is a quantity pertaining to the ideal elastic behavior, while C_2 expresses the departure from the ideal elastic behavior.

Figure 3 shows the experimental stress-strain curves given in Figure 1 replotted in the form

$$\frac{\sigma}{2(\lambda - \lambda^{-2})} \text{ vs. } \lambda^{-1}.$$

A limited linear part of the stress strain curves may be utilized to find C_1 from the intercept with the ordinate and C_2 from the slope. However, this situation may be dealt with as follows.

The tendency of paraffin wax to redistribute the carbon agglomerations is taken into account and the strain amplification factor is defined as:

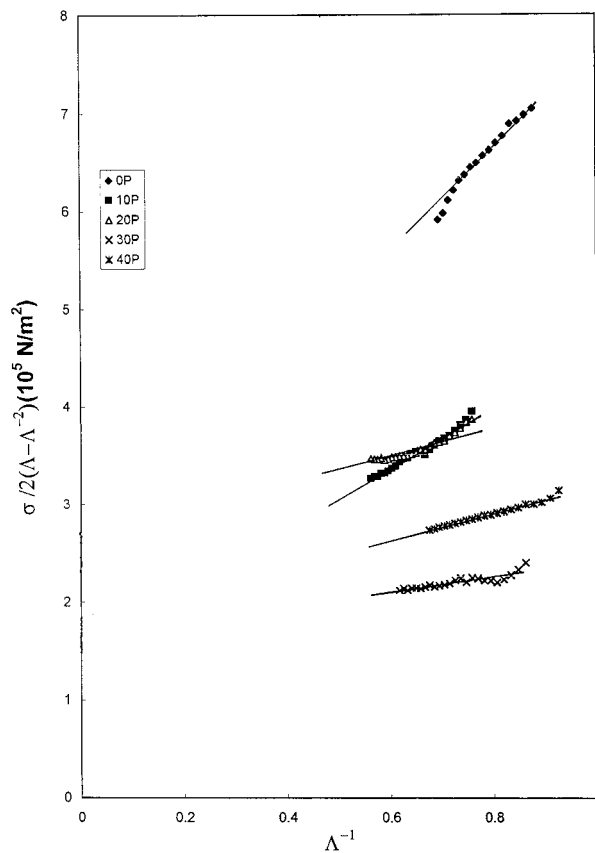


Figure 4 Stress-strain curves of Figure 3 replotted with the use of a strain amplification factor.

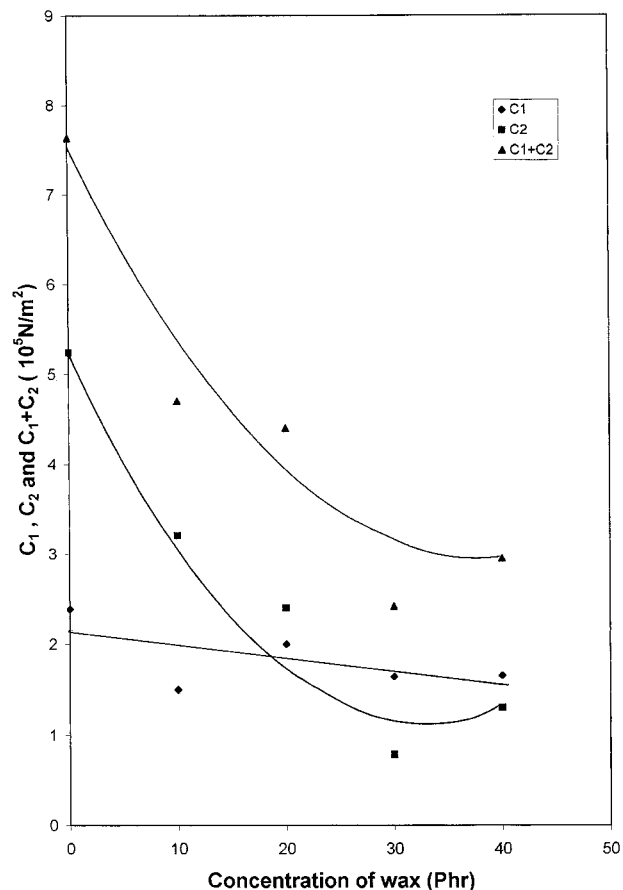


Figure 5 The dependence of C_1 , C_2 , and $(C_1 + C_2)$ on the concentration of paraffin wax for 40HAF/(SBR + NR).

$$X = \frac{\sigma}{\epsilon E_0} = \frac{E}{E_0} \quad (5)$$

where ϵ is the strain produced by a stress σ , and E_0 is the modulus of the matrix, meaning that the local strains are on the average X times greater than the overall strains. So the extension ratio λ in eq. (3) is replaced¹⁵ by $\Lambda = 1 + X\epsilon$.

Knowing the strain amplification factor given by eq. (5), the curves of Figure 3 are replotted in Figure 4 as

$$\frac{\sigma}{2(\Lambda - \Lambda^{-2})} \text{ vs. } \Lambda^{-1}$$

in the range of low strains. From these plots the constants C_1 and C_2 are readily determined, and their dependence on the concentration of paraffin wax is shown in Figure 5. The constant C_1 describes the behavior predicted by the statistical

theory of rubber-like elasticity, and its value is directly proportional to the number of network chains per unit volume of the rubber.¹⁶ The value of C_2 determines the number of steric obstructions and the number effectively trapped elastic entanglements as well as other network defects.¹⁷

In the case of high contents of wax, effects such as the isolation of network crosslinks results in the decrease of the number of networks and decrease in steric obstructions and other network defects becomes possible. These effects are manifested as a decrease in the values of C_1 and C_2 with paraffin wax, as illustrated in Figure 5.

Returning to eq. (2), again, it is noticed that the stress is a linear function of the quantity $(\lambda^2 - \lambda^{-1})$ in a moderate range of deformations. According to the experimental data in Figure 1, the tensile stress can be described as a simple function of $(\lambda^2 - \lambda^{-1})$ according to the following expression

$$\sigma = \sigma_0 + G(\lambda^2 - \lambda^{-1}) \quad (6)$$

where σ_0 is a parameter depending only on the chemical nature of the rubber matrix, and G is

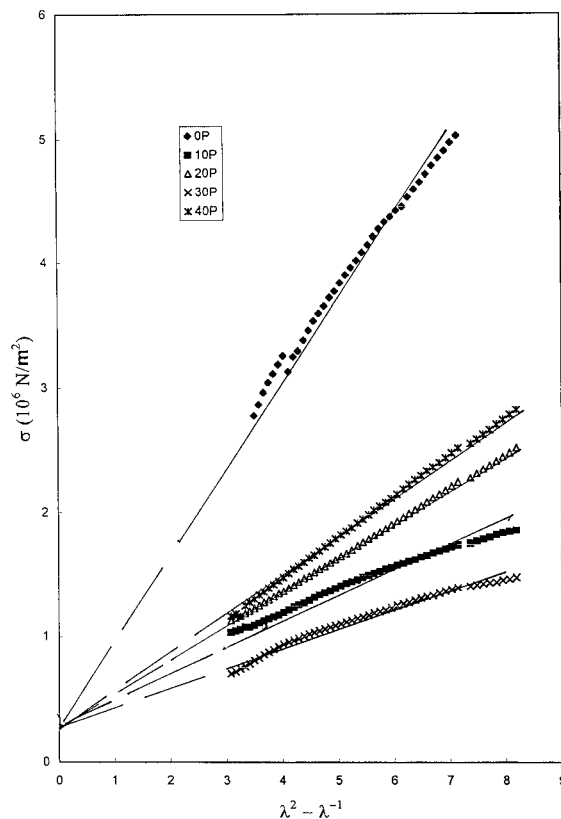


Figure 6 The dependence of the true stress on $\lambda^2 - \lambda^{-1}$ for all vulcanizates.

Table II The Calculated Values of G and σ_0 for All Studied Composites

Concentration of Wax (phr)	0	10	20	30	40
G (Pa)	6.7×10^5	1.97×10^5	2.9×10^5	1.3×10^5	3.0×10^5

the rubbery modulus of the kinetic theory that depends on the degree of crosslinking.¹³ The data in Figure 1 are replotted between the true stress and $(\lambda^2 - \lambda^{-1})$, and shown in Figure 6, where a good agreement between the theoretical solid line in the figure, which represent eq. (6), and the experimental data is clear. The interception of these lines with the stress axis at $(\lambda^2 - \lambda^{-1}) = 0$ gives the values of σ_0 , while their slopes give the values of G .

It is seen from the figure that, σ_0 has a constant value of $2.2 \times 10^5 \text{ N/m}^2$ for all used rubber vulcanizates independent on the concentration of paraffin wax. The average value of σ_0 , for both NR and SBR is about $1.05 \times 10^5 \text{ N/m}^2$ and $3.2 \times 10^5 \text{ N/m}^2$, respectively,¹³ with an average value of $2.125 \times 10^5 \text{ N/m}^2$, which is in good agreement with the value ($2.2 \times 10^5 \text{ N/m}^2$) obtained for the used matrix containing SBR and NR with equal proportions. From these discussions, σ_0 is a material constant, its value depends only on the chemical nature of the considered rubber and not on the crosslinking density or functionality. This term probably results from local interactions between chain segments, and by the way, may be related to the energy dissipated during deformation.

The values of G are listed in Table II. It is

noticed that the values of G agree well with the values of $(C_1 + C_2)$ obtained from Figure 4.

Figure 7 shows the relation between G and $C_1 + C_2$ and the concentration of paraffin wax and quite an agreement between them is observed. Figure 8, on the other hand, shows the correspondence between Young's modulus E of the vulcanizates and the values of both G and $C_1 + C_2$ determined before.

The average molecular weight M_e between crosslinks and the number of effective plastic chains per unit volume ν have been calculated from the values of G according to the equation¹³

$$G = A\nu kT = A \frac{\rho RT}{M_e} \tag{7}$$

where ρ is the density of the rubber matrix, and R is the universal gas constant. The calculated values of M_e and ν_e for all the studied vulcanized samples have been calculated assuming $A = 1$,¹³ and are illustrated in Figure 9 as a function of the concentration of paraffin wax. The figure shows a maximum average molecular weight between crosslinks for vulcanizates containing 30 phr of paraffin wax. The behavior of the number of effective plastic chains as seen

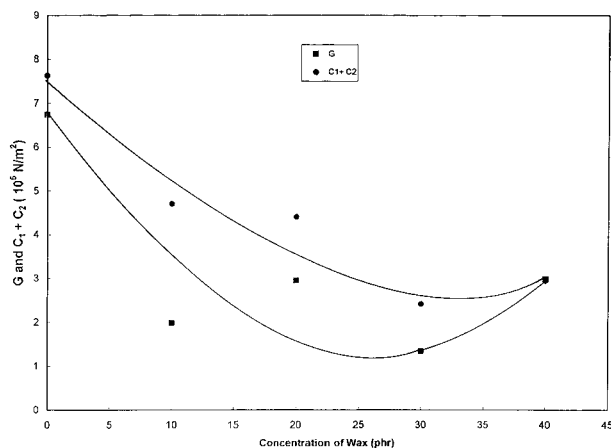


Figure 7 The dependence of G and $(C_1 + C_2)$ on the concentrations of paraffin wax.

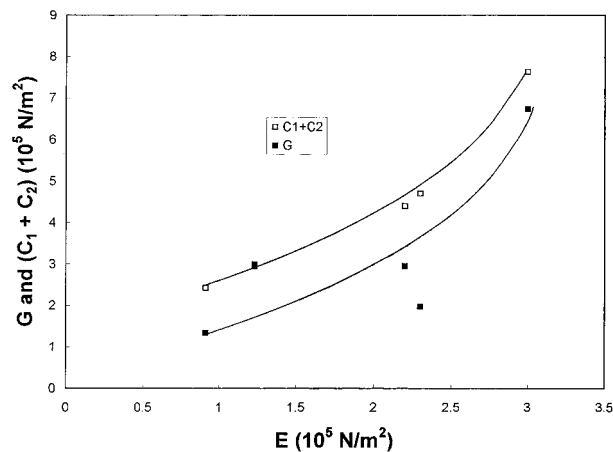


Figure 8 The dependence of G and $(C_1 + C_2)$ on Young's modulus for all vulcanizates.

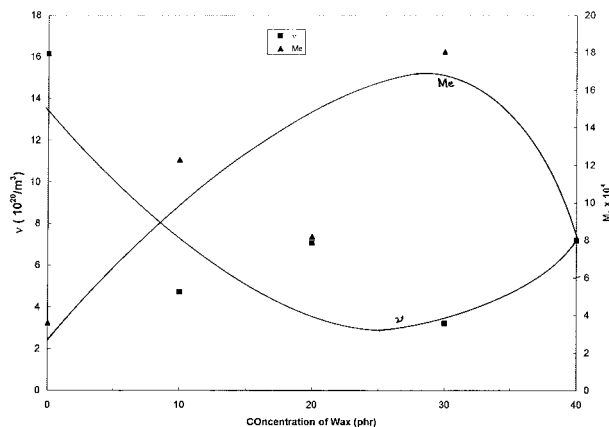


Figure 9 The dependence of ν and M_e on the concentration of paraffin wax.

from Figure 9 is opposite to that of the average molecular weight.

CONCLUSIONS

From this study one concludes that the addition of paraffin wax to an SBR–NR composite loaded with 40 phr of HAF carbon black decreases Young's modulus as a result of softening. Paraffin wax reduces also the values of C_1 , C_2 , and G as calculated using the Mooney-Revlin and Yong-Hua Zang equations, while the value of σ is independent on paraffin wax but is a parameter characteristic of the rubber. The values of $(C_1 + C_2)$ is in good agreement with the rubbery elastic modulus G , and consequently, the degree of crosslinking. The average molecular weight between crosslinks is calculated, and was found to have a

maximum for vulcanizate containing 30 phr of wax.

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REFERENCES

- Nielsen, L. E. *Mechanical Properties of polymers and Composites*; Marcel Dekker: New York, 1974, vol. 2.
- Kardos, J. L. *Crit Rev Solid State Sci* 1973, 3, 419.
- Halpin, J. C. *Primer on Composite Materials: Analysis*. Technomic: Lancaster, PA, 1984.
- Sedlacek, B. *Polymer Composites*; Walter de Gruyter: Berlin, 1986.
- Flory, P. J.; Erman, B. *Macromolecules* 1982, 15, 800.
- Erman, B.; Flory, P. J. *Macromolecules* 1982, 15, 806.
- Erman, B.; Flory, P. J. *Macromolecules* 1983, 16, 1601.
- Erman, B.; Flory, P. J. *Macromolecules* 1983, 16, 1607.
- Mullins, L.; Tobin, N. R. *J Appl Polym Sci* 1965, 9, 2993.
- Wall, F. T. *J Chem Phys* 1943, 11, 527.
- Flory, P. J. *Polymer Chemistry*; Cornell Univ Press: Ithaca, NY, 1953.
- James, H. M.; Guth, E. *J Chem Phys* 1943, 11, 455.
- Zang, Y.-H.; Muller, R.; Frolich, D. *J Rheol* 1986, 30, 1165.
- Rivlin, R. S.; Saunders, D. W. *Philos Trans R Soc* 1951, A213, 251.
- Hamza, S. S. *Mater Lett* 1997, 30, 153.
- Kontou, E.; Spathis, G. *J Appl Polym Sci* 1990, 39, 649.
- Priss, L. S. *J Polym Sci* 1975, 3, 195.