CHARACTERIZATION OF REINFORCING IN RUBBER

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Abstract

The author tries to apply a new method to characterize the reinforcing effect of fillers on basis of the Mullins softening and recovery, followed by the evaluation of the stress-elongation curves obtained after repeated deformation cycles and heat treatments of various duration. The apparent activation energy of the recovery process, i.e., the reformation of physical bonds after Mullins softening, was between 30–60 kJ/mol. It is predominantly a physical process. By the evaluation of the stress-strain curves according to the Mooney-Rivlin equation, it is established that the constant C_1 of the equation depends primarily on the number of the active network chain segments of the stable chemical network formed during vulcanization, which is also the case in filled vulcanizates. On the other hand, constant C_2 of the equation depends on the rubber-filler physical interaction, and on the number of effective network chain segments determined by chain entanglements. As these physical network point undergo changes during the deformation, the value of C_2 also changes. The constant C_2 can be used as a general parameter for the characterization of the activity, the reinforcing effect of fillers.

1. Introduction

Fillers used in the rubber industry have different effects both on the technological characteristics (rheological behaviour) of the compound and on the mechanical properties of the vulcanizates. For characterizing these reinforcing effects, generally one of the filler properties is applied. Most frequently the specific surface area, the average particle diameter of the filler, which is also mentioned as the primary structure of fillers, and the oil number which characterizes secondary structure are used to characterize the reinforcing effect. Recently lots of scientists and research workers have questioned the authenticity of the tests carried out only on fillers, saying that secondary structure (the

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level of agglomeration) changes during the different processing operations, thus, for example, the specific surface area determined by adsorption methods cannot be regarded on the whole as a rubber active surface. Chainlike rubber molecules cannot reach every holes and pores of small diameter. Therefore, in our opinion, conclusions on the reinforcing effect of different fillers can be made from properties determined in the compounds. Within the scope of this paper the stress-strain curves of SBR based vulcanizates loaded with various fillers are analyzed to determine the following factors:

—What conclusions can be drawn from the so called Mullins softening and recovery process of filled vulcanizates, and

—Is the so called Mooney-Rivlin equation used in the analysis of stress-elongation relationship of highly elastic substances, suitable for characterizing the filler activity?

2. Materials and Test Methods

In order to evaluate the reinforcing properties a compound has to be developed in which the reinforcing effect and the differences in the activity can be clearly be judged, and whose composition is close to the compounds applied in factory-scale, but relatively simple and free from the influencing effect of other compound components. For this purpose we used an SBR based compound shown in Table 1.

To evaluate the differences in the filler activities a series of carbon blacks with different primary and secondary structure were used in the investigation. For the comparison of fillers the filler quantity was kept at a constant level. Since the volume concentration is essential from the point of view of the reinforcing effect, the tests were performed at a volume fraction of $\phi=0.20$, meaning that 25 volumeparts of filler was added to 100 volumeparts of rubber. In case of the determination of the constants in the Mooney-Rivlin equation, also filler concentration series were applied.

Table 1 Used model compound

SBR 1500	100.0 phr
Filler	variable
ZnO	3.0
Stearic acid	1.0
Sulphur	1.75
CBS*	1.0

* N-cyclohexyl-2-benzthiazole-sulphenamide

Compounds were mixed in two stages. The rubber-filler masterbatch was prepared in a 2.7 liter laboratory internal mixer type Werner-Pfleiderer at a rotor speed of 40 rpm. Incorporation of sulphur and accelerator took place on a laboratory two roll mill (600×250 mm) at 50°C.

The following **test method** was used: The test specimen was stretched to 250%, then the recorder was switched off and the deformation stopped. After a short rest, when the specimen was relaxed, the second stress-strain curve has also be taken on the same diagram paper at the same deformation rate. The tests were executed on a Zwick 1445 automatic tensile tester. For deformation speed 100 mm/min was chosen, after testing its influence to the results. The specimen which was twice subjected to stretch was thereafter put to heat treatment in an unstressed state. The temperatures of the heat treatment were 70, 85, 100, 110 and 121°C.

3. The Mullins Softening and Recovery

If a vulcanized specimen is subjected to a sufficiently high deformation, e.g. it is stretched, the rubber becomes softer and a deviation appears between the stress-strain curves described with repeated stretchings. This softening can be observed with filled vulcanizates and the so called softening degree depends on the type, the quantity and also the activity of the filler. This physical phenomenon was first observed by Holt¹⁾ in the early 1930-s, but a detailed study was carried out by Mullins at the end of 1940-s²⁾. In the interpretation of the "softening phenomena", Tobin³⁾, Blanchard^{4,5)},

**SOFTENING BEHAVIOR of LOADED ELASTOMERS
according to DANNENBERG**

Fig. 1 Network-chain distribution and behaviour during stretching and relaxation in case of filled vulcanizates according to Dannenberg

Parkinson⁴⁾, as well as Bueche^{6,7)} and Dannenberg⁸⁻¹⁰⁾ were also engaged beside Mullins.

Their conclusion can be summarized as follows and is shown in Figure 1. During deformation (stretching) of the specimen, those chains being totally elongated and being incapable of carrying the load, either break or break away (dewet) from the filler surface. Chains breaking or breaking away in the first deformation cycle cannot carrying load in the second one, this causing the softening effect.

Thus the Mullins softening can be explained with the limit theory of stretchability of chains, as well as with the help of Bueche's chain distribution model. Besides softening our investigation was focused on the recovery process and on determination of its character.

3.1 Methodics of data evaluation

To follow the recovery of the Mullins softening with time, heat treatment series have been effected at all temperatures. After the heat treatment, the test specimens have been tempered at room temperature, subsequently a

Fig. 2 Effect of heat treatment on the stress-strain curves of filled vulcanizates
 Temperature of heat treatment: 110°C
 Filler: HAF black

stress-strain curve was taken again according to the method described above.

A few characteristics curves of HAF black (N330) containing vulcanizates are shown in Figure 2. The continuous line represents the stress values obtained during the first and second deformation (stretching), the dotted curves however give the stress-strain relationship after definite heat treatment periods.

At two selected deformation values at 100 and 200% of stretching ($\lambda=2$ and $\lambda=3$) the stress development belonging to the given deformation has been examined. As can be seen from Fig. 1, which is displaying the recovery process and the evaluation method, the stress results belonging to the given stretch of the test specimen differ from one another. Stress values belonging to the given deformation are denoted by σ_1 and σ_2 :

σ_1 = stress value obtained during the first deformation cycle, MPa

σ_2 = stress value obtained during the second deformation cycle, MPa

Softening is denoted by p :

$$p = \sigma_1 - \sigma_2 \quad (1)$$

Considering that the relative value of softening is essential from the viewpoint of recovery, the Pr value has been introduced.

$$p_r = \frac{\sigma_1 - \sigma_2}{\sigma_1} \times 100\% \quad (2)$$

Upon heat treatment, the extent of softening decreased and a recovery could be observed,

$$\sigma_{T,t} > \sigma_2 \quad (3)$$

Where $\sigma_{T,t}$ means the stress value belonging to a given deformation of the sample heat treated for a period of t at a temperature of T .

Softening retention after heat treatment:

$$p_r = \frac{\sigma_1 - \sigma_{T,t}}{\sigma_1} \times 100\% \quad (4)$$

At higher heat treatment temperatures (110, 121°C) under higher deformation (λ) values and after longer heat treatment procedures, it

has been repeatedly observed that the stress values measured after the heat treatment exceeded the starting stress value. In this case $\sigma_{T,t} > \sigma_1$, thus a negative softening, i.e. "hardening" took place. As I later show, it is due to the rearrangement of the chain distribution function.

The next step of data evaluation was the **determination of the temperature and time dependence** of the softening-recovery. For this purpose, primarily the relative softening value p_r has been plotted against time on compounds prepared with different fillers. It was then examined how far the recovery satisfied the exponential characteristics, by use of the following relation for the time dependence of softening-recovery:

$$p_r = A e^{-kt} \quad (5)$$

Taking the logarithm of both sides:

$$\ln p_r = \ln A - kt \quad (6)$$

Test results have been plotted, based on Eq. (6). Experimental point obtained approximately fell within the straight lines, and by reading their slope the softening recovery constant (k) was obtained at the temperature examined. Characteristic test data series are displayed in Figure 3. This Figure illustrates the softening recovery of compounds prepared with different carbon blacks after heat treatment at 100°C.

The recovery rate constants at different temperatures permit us to determine the **apparent activation energy** of the recovery process, i.e. of the new rubber-filler bond development. For this use of the Arrhenius equation has opened opportunities:

$$k = A \exp \left(-\frac{E_a}{RT} \right) \quad (7)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (8)$$

where: E_a = activation energy

k = reaction rate constant

A = preexponential factor

R = universal gas constant

T = absolute temperature

Fig. 3 Determination of the recovery rate constant (k) on the basis of relative softening data for vulcanizates containing different carbon black types

Fig. 4 Temperature dependence of the recovery rate constant (k) in case of different carbon black types

It can be seen from Figure 4, that the slopes of straight lines obtained for the individual black types, though very close to one another, increased from lamp black to ISAF black. This means that in the same direction—i.e. moving to more active blacks—the virtual activation energy of

Table 2 Apparent activation energies obtained for the softening-recovery process

Filler	E_a (kJ/mol)	
	A ($\lambda=2$)	B ($\lambda=3$)
ISAF	53.1	52.2
HAF	48.1	46.3
FEF	45.5	43.1
SRF	40.5	38.1
Lamp black	33.9	33.1

the softening recovery process also increased.

3.2 Character of the recovery process

Table 2 contains the activation energy values calculated from the slopes of the straight lines read from Figure 4. A and B mean the two calculation points, mainly $\lambda=2$ and $\lambda=3$.

It can be seen from the data that recovery takes place upon heat treatment, that is, the repeated development (the reformation) or rubber-filler interaction is decisively a physical process, its virtual activation energy being 30–60 kJ/mol as a function of the filler type.

4. Stress-Strain Curves and The Mooney-Rivlin Equation

For the characterization of non-ideal rubber networks the most widely used equation is the phenomenological Mooney-Rivlin equation. It is a result of historical development in the description of rubber elasticity. The first remarkable molecular interpretation of rubber elasticity was introduced by Kuhn, Guth and Mark in the 1930-s^{11,12)}. They studied idealized rubber networks on the basis of various assumptions. They described the configuration and conformation of the monomeric unit and developed the statistical mechanics of polymer chain. In the Gaussian chain model, where the end-to-end distance of the chain results in a Gaussian distribution function, the elastic forces are calculated from the conformational entropy loss of the network chain, when the end-to-end distance deviates from its most probable value. If the theory is correct during stretching of rubber the reduced stress should be independent of

Fig. 5 The Mooney-Rivlin relation for vulcanizates filled with carbon blacks of different types

elongation (λ). Real rubber deviates from the theory^{13,16)}.

Later other approaches and theories have been developed for the description of the real stress-strain behavior of amorphous polymer networks. Essentially additional assumption concerning the influence of the surrounding chains on the entropy of a single network chain were made. Flory¹⁴⁻²⁰⁾, Erman¹⁹⁾, Kaestner²¹⁻²³⁾ and Tschoegel²⁴⁾ developed a concept of restricted junction fluctuation, while the network chains were handled as phantom chains, which do not feel any constrain. Rivlin described the behavior of rubber network on the basis of strain energy function¹³⁾. A new realistic approach to the consideration of topological constrains in real polymer network are the tube model, and the slip-link model²⁵⁻³¹⁾. The limited space does not allow the author the detailed discussion of these network models.

This short historical review shows us the complexity of rubber elasticity. The presence of fillers in the polymer networks makes the mathematical interpretation more complex and difficult. We focused our research work to the description of the Mullins softening with the Mooney-Rivlin equation and to the determination and interpretation of the C_1 C_2 constants of the equation.

Table 3 C_1 and C_2 constants of the Mooney-Rivlin equation for vulcanizates filled with different carbon blacks

$\phi = 0.20$		C_1 and C_2 (MPa)			
		1. deformation cycle		2. deformation cycle	
Filler		C_1	C_2	C_1	C_2
SAF	N110	0.26	1.04	0.23	0.40
ISAF	N220	0.21	1.03	0.18	0.49
ISAF	N220	0.19	0.89	0.16	0.46
ISAF-HM	N220	0.25	0.91	0.24	0.40
ISAF-HS	N242	0.20	0.96	0.19	0.46
HAF	N330	0.24	0.72	0.21	0.31
HAF	N330	0.18	0.86	0.15	0.47
HAF	N330	0.19	0.82	0.19	0.45
HAF-LS	N326	0.20	0.64	0.18	0.34
HAF-HS	N347	0.24	0.84	0.24	0.37
HAF-HS	N347	0.22	0.92	0.15	0.52
HAF-imp	N339	0.18	0.90	0.16	0.47
HAF-imp	N375	0.23	0.87	0.22	0.36
FEF	N550	0.25	0.79	0.25	0.50
FEF	N550	0.22	0.70	0.14	0.51
FEF	N539	0.18	0.72	0.14	0.47
GPF	N660	0.21	0.69	0.19	0.43
GPF	N660	0.22	0.64	0.19	0.48
APF	N683	0.25	0.67	0.22	0.33
SRF-HS	N765	0.24	0.60	0.24	0.38
SRF-HS	N765	0.24	0.72	0.20	0.36
SRF-HM	N774	0.25	0.49	0.24	0.32
SRF-HM	N774	0.26	0.57	0.18	0.40
SRF-LM	N762	0.18	0.54	0.16	0.38
LB	Lamp Black	0.18	0.43	0.12	0.31
MT	N990	0.14	0.40	0.12	0.33
Acetilen Black	—	0.16	0.77	0.17	0.57
Unfilled		0.13	0.17	0.12	0.16

4.1 Evaluation of the stress-strain curves according to the Mooney-Rivlin equation

Analyzing numerous stress-strain curves has lead us to evaluate them using the Mooney-Rivlin equation in order to elucidate the Mullins softening.

$$\sigma = 2 \left(C_1 + \frac{C_2}{\lambda} \right) \cdot \left(\lambda - \frac{1}{\lambda^2} \right) \quad (9)$$

For this purpose the equation was rearranged as:

$$\frac{\sigma}{2 \left(\lambda - \frac{1}{\lambda^2} \right)} = C_1 + \frac{C_2}{\lambda} \quad (10)$$

Thereafter the points (i.e. the stress values

belonging to the given deformations) were taken according to the rearranged equation. The next step was to draw the best fit straight lines to the data series. The intercept to the straight line is C_1 , and its slope determines the constant C_2 . The constant C_1 and C_2 were determined for both the first and second deformation cycles. For demonstrating the differences between compounds containing different types of fillers in Figure 5 the curves of a few blacks are illustrated.

The values of C_1 and C_2 are summarized in Table 3, which contains the data of vulcanizates filled with various carbon blacks. (Where the same type is listed more than once, when the

Fig. 6 The Mooney-Rivlin relation as a function of filler volume fraction for vulcanizates filled with HAF black

Fig. 7 Constant C_2 as a function of the filler volume fraction for different fillers

producer is different).

4.2 Role of filler volume concentration

The extent of reinforcing effect depends on both filler type and its concentration. Therefore the next step was the determination of concentration dependence of constant C_1 and C_2 . For this purpose three carbon black types (HAF, FEF, SRF) and a white active filler (precipitated silica) were selected.

The volume concentration series (volume fraction) varied as follows:

$$\phi = 0.05; 0.10; 0.15 \text{ and } 0.20$$

The course of Mooney-Rivlin curves in cases of a given black is illustrated in Figure 6.

In order to examine the proper relation between C_2 and the volume fraction of filler (ϕ), we plotted C_2 values as a function of volume fraction ϕ . It can be seen from Figure 7, that this relation is practically linear for all fillers tested. The slope of the straight lines differs to a given extent. The slopes of the three carbon black types increase with growing activity.

It can also be established from Figure 7 that the C_2 value extrapolated to $\phi=0$ filler concentration is in a good agreement with the C_2 value actually obtained for unloaded compounds (See Table 3 and Figure 5).

4.3 Evaluation of the Mullins recovery according to the Mooney-Rivlin equation

As discussed in chapter 3., we can

characterize the Mullins recovery process by a set of curves obtained after heat treatment at different temperature and duration. It means that it is possible to elaborate the whole Mullins softening and recovery process on the basis of the Mooney-Rivlin equation. In order to establish what changes can be observed in the Mooney-Rivlin curves and especially in the characteristic constants C_1 and C_2 we transformed the original stress data to the reduced form of Mooney-Rivlin. The experimental data in case of an ISAF carbon black are illustrated in Figure 8.

From the Figure, it seems to be clear that the Mullins recovery can be characterized by a set of curves (lines) starting from a practically common intercept C_1 , while the slope of the straight lines increases as a function of the heat treatment time. (Had we chosen the heat treatment time constant, as a function of the heat treatment temperature.) At higher heat treatment temperatures and under longer heat treatment times, the slope C_2 can exceed the C_2 value obtained for the first deformation cycle.

4.4 Experimental analysis of the constants C_1 and C_2

After analyzing the results the following conclusions could be drawn for the Mooney-Rivlin constants C_1 and C_2 :

Fig. 8 Interpretation of Mullins softening and recovery with the Mooney-Rivlin relation (ISAF black containing vulcanizates)

Constant C_1 :

(1) C_1 values obtained for filled vulcanizates during the first deformation cycle do not significantly differ from one another. Although the C_1 value for unfilled vulcanizate is slightly lower than the same values for filled ones, and an increasing tendency is visible toward the more active fillers, this tendency is only slightly pronounced (Table 3).

(2) C_1 value increases to a very small degree as a function of filler volume concentration.

(3) During repeated stretching, i.e. Mullins softening, and also during the recovery process, the intercept of the Mooney-Rivlin straight lines is practically unchanged, and it is impossible to observe any drastic decrease in the C_1 values. (Only small drops were registered, see Table 3 and Figure 8).

Constant C_2 :

(4) On the contrary to C_1 values the C_2 values obtained for the first deformation cycle differ from one another to a significant extent. The two limiting values are 0.17 for the unload compound, and 1.04 for the SAF black containing compound. On examining the data it appears at first sight that C_2 i.e. the slope of the Mooney-Rivlin straight line increases from the

inactive carbon blacks (MT) to active blacks (HAF, ISAF, SAF).

(5) C_2 value strongly or appreciably increases for the filler type tested as a function of filler volume concentration.

(6) A considerable change in C_2 takes place during both the second deformation cycle and the heat treatment procedure. During the second deformation cycle C_2 decreases in every loaded vulcanizate, and the extent of changes is more enhanced in case of active fillers. After the Mullins softening the Mooney-Rivlin lines do not differ to a such large extent as before the stretching.

(7) The Mullins softening recovery process, i.e., the rebuilding of the rubber-filler physical interaction, can be characterized by a set of curves differing in the C_2 values.

5. Characterization of Filled Nonideal Rubber Networks By Stress-Strain Curves

The properties of unfilled rubber vulcanizates (amorphous rubber networks), including the stress pertaining to a given deformation, are mainly governed by the degree of crosslinking, and by the number of active network chain segments (ν_p) occurring in volume-unit and terminating on both ends at the points

Fig. 9 Schematic representation of a nonideal network by Klueppel (a, b) dangling free chain ends, (b) temporary entanglements, (c) trapped entanglements, (d, e) elastically effective and ineffective close loops

of junction. Besides the active network chain segments formed during vulcanization, also the so called trapped entanglements (ν_{ent}) have to be counted as the elastically effective chains, which are illustrated in Figure 9 on the basis of Klueppel³¹⁾.

The behaviour of filled system deviates so far from that of unfilled ones, that due to rubber-filler interaction, besides the actual vulcanization network points and trapped entanglements, the creation of virtual (filler-rubber) network points has to be assumed, that is, the total number of active network chain segments increases with (ν_f).

$$\nu_{\text{eff}} = \nu_p + \nu_{\text{ent}} + \nu_f \quad (11)$$

where: ν_{eff} = number of all network chain segments,

ν_p = number of active network chain segments developing during vulcanization

ν_{ent} = number of active network chain segments due to entanglements

ν_f = number of active chain segments due to the rubber-filler interaction

On the basis of this investigation we come to the conclusion, that the physical meaning of constant C_1 in the Mooney-Rivlin equation is decisively determined by the number of active network chain segments in elastomer developing during vulcanization, i.e. C_1 is dependent on ν_p . A certain contribution to C_1 involves also the stable active chain segments developed by the reaction of the functional group occurring on the surfaces on rubber and filler.

$$2C_1 = \nu_p RT \quad (12)$$

This is proved by the fact that C_1 has almost the same value for different furnace blacks, meaning that the crosslinking process of elastomer and the density of the developing network is not changed by incorporation of carbon black.

Constant C_2 (slope) is proportional to the number of changing (destroying and newly developing, as a function of load and temperature) active network chain segments, i.e. to ν_f , due to the rubber-filler interaction and to ν_{ent} due to the entanglement.

$$\text{In case of active fillers: } \nu_f \gg \nu_{\text{ent}} \quad (13)$$

It is possible to give an explanation also on the basis of the chain (segment) distribution function. Upon incorporating the filler, with developing rubber-filler interaction, the distance changes among the chain-ends and junction point of the active network chain segments. In the filled system such a state is established that the distance between the chain ends differs already at smaller deformation from the Gaussian distribution function. In this approach C_2 gives the deviation degree from the ideal Gaussian distribution function. Already unfilled amorphous rubber networks usually deviate from the "ideal" state. This deviation is increased however by the adding filler to the elastomer matrix as a result of rubber-filler interaction, the magnitude of which can be characterized by ν_f that is, again the conclusion can be drawn that C_2 is proportional to ν_f .

6. Characterization of Filler Activity

The original goal of our investigation was

Fig. 10 Relation between surface area characterized by the iodine-adsorption and the constant C_2 obtained from the Mooney-Rivlin equation

Fig. 11 Relation between the oil-number and the constant C_2 obtained from the Mooney-Rivlin equation

to examine the possibilities of proper characterization of the reinforcing effect. The picture would not be complete without examining the dependence of constant C_2 on the traditional filler characterizing values (properties), that is on the specific surface area (iodine number) and the secondary structure (oil number). For this purpose the C_2 value was plotted against the iodine adsorption (Figure

10) and the DBP-absorption (Figure 11) measured for the fillers.

From Figure 10 it can be clearly seen that C_2 value increases with the specific surface area characterized by the iodine adsorption. According to our consideration this dependence can be more characterized by a curve of decreasing slope, than with a straight line. Thus the C_2 value justifies the experimental knowledge that

on increasing the specific surface area beyond certain limits no further increase in the reinforcing effect can be observed. Based on the figure it is easy to segregate the different filler types (SRF, GPF, FEF, HAF, ISAF, SAF) from one another.

A similar relation is illustrated in Figure 11, too, in which the development of C_2 can be seen as a function of secondary structure. Also here carbon blacks of different types and structures can clearly be separated from one another. It can further be established that C_2 is unequivocally increased by an extensive secondary structure.

Based on the result it can be established that by plotting the stress-strain relation according to the Mooney-Rivlin equation, a characteristic constant can be derived, which involves the effect of both the filler specific surface and its secondary structure. Thus it is suitable for characterizing the reinforcing effect within a given filler group.

Acknowledgement

The author is indebted especially to Professor Peter Szor (Budapest, Hungary) who suggested and later stimulated to start this research project, furthermore to Professor J. B. Donnet (Mulhouse, France) for his scientific support and to Professor Yoichi Nagase (Hiroshima University, Japan) for the fruitful discussions during the interpretation of the results.

References

- 1) Holt, W. L.: *Rubber Chem. Technol.*, **5**, 79 (1932)
- 2) Mullins, L.: *Rubber Chem. Technol.*, **21**, 281 (1948)
- 3) Mullins, L., Tobin, N. R.: *Rubber Chem. Technol.*, **30**, 555 (1957)
- 4) Blanchard, A. F., Parkinson, P.: *Ind. Eng. Chem.*, **44**, 799 (1952)
- 5) Blanchard, A. F.: *J. Polymer Sci.*, **14**, 355 (1954)
- 6) Bueche, F.: *A. Appl. Polymer Sci.*, **4**, 107 (1960)
- 7) Bueche, F.: *A. Appl. Polymer Sci.*, **5**, 271 (1961)
- 8) Dannenberg, E. M., Brennan, J. J.: *Rubber Chem. Technol.*, **39**, 597 (1966)
- 9) Dannenberg, E. M.: *Trans Inst. Rubber Ind.*, **42**, 26 (1966)
- 10) Dannenberg, E. M.: *Rubber Chem. Technol.*, **48**, 410 (1975)
- 11) Kuhn, W.: *Kolloid Z.*, **68**, 2 (1934); **76**, 258 (1936); **87**, 3 (1939)
- 12) Guth, E., Mark, H.: *Monatsh. Chem.*, **65**, 93 (1934)
- 13) Treloar, L. R. G.: *The Physics of Rubber Elasticity*, 3rd ed., Claderon Press, Oxford, (1975)
- 14) Flory, P. J.: *Chem. Rev.*, **35**, 51 (1944)
- 15) Flory, P. J.: *Principles of Polymer Chemistry*, Cornell University, Ithaca, NY (1953)
- 16) Flory, P. J.: *Statistical Mechanics of Chain Molecules*, Wiley, New York (1969)
- 17) Flory, P. J.: *J. Chem. Phys.*, **66**, 5720 (1977)
- 18) Flory, P. J.: *Polymer*, **20**, 1317 (1979)
- 19) Flory, P. J.; Erman, B.: *Macromolecules*, **15**, 800 (1982)
- 20) Flory, P. J.: *Polym. J.*, **17**, 1 (1985)
- 21) Kaestner, S.: *Polymer*, **20**, 1327 (1979)
- 22) Kaestner, S.: *Acta Polym.*, **31**, 444 (1980)
- 23) Kaestner, S.: *Colloid Polym. Sci.*, **259**, 499, 508 (1981)
- 24) Tschoegel, N. W.: *Proc. 9th Europhys. Conf. Macromol. Phys.*, Jablonna, Poland, (1979)
- 25) Heinrich, G.; Straube, E.; Helms, G.: *Acta Polym.*, **31**, 275 (1980)
- 26) Heinrich, G.: *Plaste Kautsch.*, **29**, 437 (1982)
- 27) Heinrich, G.; Straube, E.: *Acta Polym.*, **35**, 115 (1984)
- 28) Heinrich, G.; Straube, E.; Helms, G.: *Adv. Polym. Sci.*, **85**, 33 (1988)
- 29) Edwards, S. S.; Vilgis, T. A.: *Rep. Prog. Phys.*, **51**, 243 (1988)
- 30) Vilgis, T. A.: *Kautsch. Gummi Kunstst.*, **42**, 475 (1989)
- 31) Klueppel, M.: *J. Appl. Polym. Sci.*, **48**, 1137 (1993)