Ultrasonic and Mechanical Measurements for the Detection of Crosslink Density of SBR and NBR Based on Various Curing Systems

S. N. Lawandy,[1] **S. F. Halim,**[1] **H. A. Afifi**[2]

[1]*Laboratory of Metrology and Technology of Polymer, National Institute of Standards (NIS), Giza, Egypt*
[2]*Laboratory of Ultrasonic Metrology, National Institute of Standards (NIS), Giza, Egypt*

ABSTRACT: The stress–strain measurements of styrene-butadiene rubber (SBR) samples based on various curing systems were used to access the crosslink density of various rubber mixes. Same materials were subjected to various uniaxial compression strains. The thicknesses before compression and after recovery were recorded. After recovery, pulse echo method was used to measure the ultrasonic velocity for the dilatational wave and that of shear wave at a frequency of 2 MHz and at room temperature. Both of the ultrasonic velocities were used to determine the elastic moduli of the samples. The relation between the elastic moduli and the corresponding recovery values were used to determine the crosslink density of samples. The crosslink density values obtained from the two techniques were compared. Butadiene-acrylonitrile (NBR) rubber mix was used to show that the ultrasonic technique is applicable for other rubber compounds. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 366–371, 2009

Key words: curing of polymers; crosslinking; compression; vulcanization; network

INTRODUCTION

Two factors are very important in the vulcanization of rubber: (i) the density of crosslinking (the frequency with which a rubber chain is linked to others); (ii) the nature of crosslink. Sulfur is the common and most generally used crosslinking agent.

Its action is controlled by organic accelerator systems, of which there is a wide choice, and an activating system commonly supplied by zinc oxide in the presence of stearic acid. The normal sulfur vulcanization system is capable of many variants, which will govern the number of crosslink produced and the chemical nature of sulfur crosslink, that is, whether it is essentially a mono-, di- or poly sulfidic type.[1] The acceleration to sulfur ratio variation affects the crosslink density which in turn influence to a great extent the rubber vulcanizates properties.

In the literature, several methods were used to access the crosslink density of rubber vulcanizates. Manik and Banerjee[2] found that both the Flory equation as well as other equations relating chemical crosslinks to physical ones can be satisfactorily employed for the calculation of chemical crosslinks from the physical crosslinks determined by swelling measurements. Swelling methods and stress–strain analysis were used to determine the crosslink density of the rubber network.[3–8] Vennemann et al.[9] examined temperature scanning stress relaxation (TSSR) to determine the crosslink density of EPDM/PP compounds. These results were in good agreement with the results obtained from conventional swell measurements, which is very time-consuming. Hergenrother[10] used the tensile retraction measurements to determine the molecular weight between two crosslinks in a vulcanized SBR.

The ultrasonic technique was successfully used as a tool to investigate many polymeric properties.[11–13]

However, in our previous work,[14] the crosslink density of various nitrile mixes was calculated using the kinetic theory of elasticity. In this study, we are trying to calculate the crosslink density of SBR vulcanizates, containing different vulcanizing system, by stress–strain measurements and ultrasonic technique.

EXPERIMENTAL

Materials

The mixes examined were based on SBR, Koyson 1502, supplied by Korea Kumho petrochemical company, its Mooney viscosity ($ML_1 + 4$) at 100°C was 51.8 and the content of bound styrene was 23.3 mass %, and Butadiene-acrylonitrile rubber, Krynac 40/50, supplied by Polysar, France. Tetramethyl thiuram disulphide TMTD, *N*-cyclohexyl benzthiazyl

<div align="center">

TABLE I
Formulation of SBR Rubber Mixes and Rheometric Properties

</div>

Ingredient/sample No.	CV1	CV2	CV3	Semi-EV1	Semi-EV2	Semi-EV3	EV	TMTD
SBR	100	100	100	100	100	100	100	100
Zinc oxide	3	3	3	3	3	3	3	3
Stearic acid	2	2	2	2	2	2	2	2
Processing oil	5	5	5	5	5	5	5	5
SRF	20	20	20	20	20	20	20	20
Sulpher	2.5	2	2	1.75	2	2	1	–
CBS	0.75	0.75	1.25	1	1.5	1.75	1.5	–
DPG	0.25	0.25	–	0.8	–	–	0.75	–
TMTD	–	–	–	–	0.25	–	–	3
Rheometric properties								
Maximum torque, lb-in	2.09	8.97	2.10	4.39	9.5	2.5	4.32	4.55
Minimum torque, lb-in	0.74	0.72	0.74	0.77	0.72	0.74	0.79	0.7
Scorch time (min)	19.66	%%	30.16	13.87	5.58	36.78	19.42	2.43
Cure time, t_{90}	22.95	20.13	36.27	36.16	20.56	54.6	53.26	8.29

sulfinamide CBS, diphenyl guanidine DPG, and sulfur S were added as curing agents with different concentrations to prepare rubber compounds of various degree of crosslinking. Carbon black SRF and GPF were used as fillers. The rubber mixes were prepared using two-roll mill at a friction ratio 1 : 1.25. The optimum curing time for each mix at 152°C was estimated using Monsanto rheometer. The mix formulations are given in Tables I and II.

Stress–strain measurements

Dumpbell-shape samples were prepared according to ASTM D412-98a and were used for relaxed stress–strain measurements. The Zwick tensile testing machine model Z010 was run at a speed of 10 mm/min. The tests were run up to 16% strain. From the recorded data, the extension ratios $\lambda = l/l_o$ were calculated. For each value of λ, the corresponding

<div align="center">

TABLE II
Formulation of NBR Rubber Mix and Some Mechanical Properties

</div>

Ingredient	
NBR 40/50	100
Zinc oxide	5
Stearic acid	1.5
Peptizer[a]	10
GPF black	10
Non oiled Sulpher	2
CBS	1
6PPD	3
Resorcinol	2
Vulcasil H[b]	1.2
Silica	5
Mechanical properties	
Cure time, t_{90}	10
Tensile Strength (MPa)	10
Elongation at break (%)	509
Hardness, Shore A	51

[a] Pentachlorothiophenol.
[b] Hexamethylenetetramine.

value $(\lambda - \lambda^{-2})$ was calculated and plotted against the applied stress F/A_o.

Compression recovery measurements

Same mixes used for the stress–strain measurements were used to prepare cylindrical samples of dimension 13-mm diameter and 10-mm thick, which were molded at the same conditions of temperature and time recorded before by the rheometer. A compression set clamp device was used to accommodate the different mixes at the same time. The device consists of six steel plates between which the test pieces are compressed. The plates are held together by a bolt. Spacers of different thickness are placed around the axial bolt. The ring form spacers are of different heights to limit the degree of compression. After placing the samples in between the steel plates, the bolt was tightened until the plates are in contact with the spacers. Clamping the samples was carried out for 48 h in an air circulating oven at 100°C. The device was left to cool; then, samples were released and allowed to recover for half an hour before measuring the thickness accurately. The thickness before and after compression are denoted as d_0 and d, respectively.
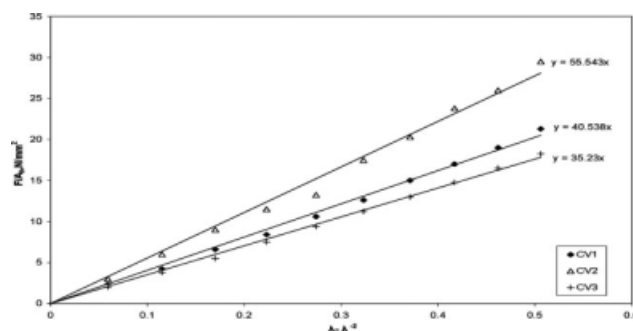

Figure 1 Stress–strain curves for rubber mixes containing conventional (CV) vulcanizing systems.

TABLE III
Some Physical Properties of SBR Vulcanizates

Property/Sample No.	CV1	CV2	CV3	Semi-EV1	Semi-EV2	Semi-EV3	EV	TMTD
Tensile Strength ($\pm$0.4) (MPa)	6.21	10.53	1.55	7.60	9.46	3.74	11.2	7.84
E-modulus ($\pm$0.36) (MPa)	0.85	1.96	1.16	1.09	1.87	1.46	0.95	0.94
Elongation at break ($\pm$30) (%)	2897	1241	3152	1627	1157	2766	2027	1948
Hardness ($\pm$0.5), Shore A	28.7	46.90	27.6	37.7	48.00	30.90	38.3	37.1

Ultrasonic principle, system and method of detection

The ultrasonic waves can be generated from periodically vibrating piezoelectric transducer propagating the samples. There are four types of ultrasonic waves, namely longitudinal wave, shear wave, Rayleigh wave, and Lamb wave. The longitudinal wave is often preferentially utilized to characterize many polymeric properties. In this study, the ultrasonic measurements were carried out using ultrasonic flaw detector (USIP 20), an oscilloscope (54615B), longitudinal transducer (central frequency of 0.50 MHz and band width of 1 MHz), and shear transducer (central frequency of 0.45 MHz and band width of 0.9 MHz). Incident waves were transmitted in a sample of thickness, d, and reflected back and forth at the two surfaces. When the reflected wave reaches the upper surface and received by the transducer, an echo signal containing several oscillations will be gained. A series of echo signals can be obtained as ultrasonic waves reflected between the two surfaces. However, the amplitudes of the echo signals are gradually decreased with time due to ultrasonic attenuation. The first two echo signals, of amplitudes (A_1, A_2) and corresponding time (t_1, t_2) can be read and chosen to calculate the velocity.[15]

$$V = 2d/t_2 - t_1$$

The measurements of ultrasonic velocities (longitudinal, shear) were repeated three times to check the reproducibility of the data. The estimated accuracies are about 0.02 and 0.03%.

The calculated values of V were used to calculate the longitudinal modulus (L) and shear modulus (G) using the following equations:[15]

$$L = \rho V_l^2, \quad G = \rho V_s^2$$

where V_l, V_s are the longitudinal and shear ultrasonic velocities, ρ is the rubber density. Subsequently, Poisson's ratio (σ) and Young's modulus (E_y), were calculated using the following equations:[15]

$$\sigma = (L - 2G)/2(L - G)$$

$$E_y = 2G(1 + \sigma)$$

RESULTS AND DISCUSSION

Three different vulcanizing systems were used in SBR rubber mixes. These are conventional (CV), efficient (EV), and semi-efficient vulcanization (semi-EV) were employed in this study to obtain various distribution of c-s$_x$-c sulfidic crosslinks of various ranks x and different crosslink structure. In the CV system, higher sulfur to accelerator ratio is selected, and in the EV system, low sulfur to accelerator ratio is selected.[16] An intermediate accelerator to sulfur ratio of 1 : 1 is typical of a semi-EV system. Because of higher content of sulfur in the CV system predominately polysulfidic linkages are formed in the CV system. On the other hand, predominately mono and disulfidic linkages are formed in the EV system, which are due to higher accelerator content.[17] To widen the range of crosslinking TMTD, as an accelerator and vulcanizing system, was used alone as a

TABLE IV
M_c Values and Crosslink Density of Different Rubber Vulcanizates

Sample	M_c value (g mole^{-1})		Crosslink density $\times$ 10^{-4} (g^{-1} mole)	
	Stress-strain	Ultrasonic	Stress-strain	Ultrasonic
CV1	5989.7	5936.6	0.8348	0.8422
CV2	4371.6	4662.3	0.1144	0.1072
CV3	6892.2	6746.6	0.7255	0.7411
Semi-EV1	4921.9	4936.2	0.1016	0.1013
Semi-EV2	4441.6	4859.2	0.1126	0.1029
Semi-EV3	7220.3	6835.9	0.6925	0.7314
EV	4812.1	4967.5	0.1039	0.1007
TMTD	4240.6	4417.7	0.1179	0.1132
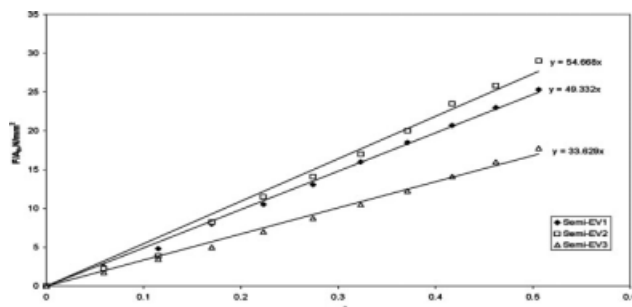
Figure 2 Stress–strain curves of rubber mixes containing semi-efficient vulcanizing systems (semi-EV).

Figure 4 Relation between E_y and $1 + d/d_0 + (d/d_0)^2$ for mixes containing conventional (CV) vulcanizing systems.

sulfur less vulcanizing system which gives mainly mono-sulfidic linkage.

The mechanical properties of the various SBR rubber vulcanizates used in this study were measured and reported in Table III; and their M_c values and crosslink density are given in Table IV. It is clear that the crosslink density in the rubber network is not always an indication of certain trend in the mechanical properties. The reason is that the network chain is not only a function of crosslinks. There may be for the whole network twice as many network chains as crosslinks. These additional networks may be caused by the type of functionality formed during accelerated sulfur vulcanization, the density of entanglement and the vulcanizate chain ends.[18]

The stress–strain measurements have been used to evaluate the crosslink density of rubber compounds based on different curing systems. This evaluation is based on the statistical theory of rubber like elasticity.[19–21] The theory relates the force applied (F) per unit area (A_0) required to strain a perfectly elastic network at a small extension ratio (λ) is given by:

$$F/A_0 = \frac{\rho RT}{M_c}\left(\lambda - \lambda^{-2}\right) = 2C_1\left(\lambda - \lambda^{-2}\right) \text{ dyne/cm}^2 \quad (1)$$

where ρ is the density of rubber, T is the absolute temperature, R is the gas constant and M_c is the molecular weight between two crosslinks. It is interesting to note here that the $R = 8.3143 \times 10^7$ gm cm^2/

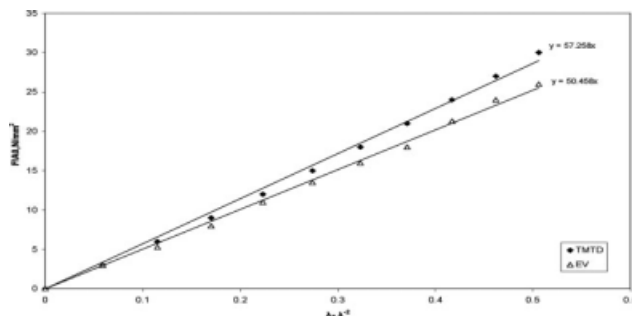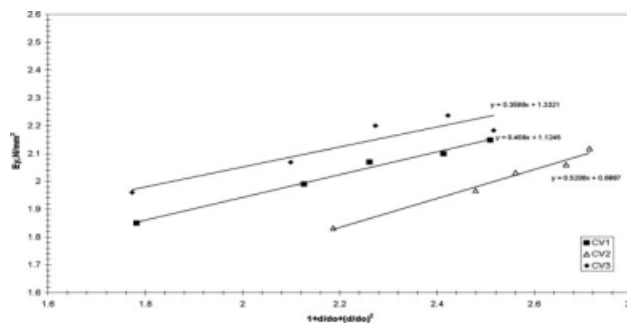s^2 deg^{-1}mol^{-1} and that the crosslink density is $1/2$ M_c gm mol^{-1}.

Mooney and Rivilin[22] modified eq. (1) to give another expression. This expression is:

$$F = 2A_0\left(\lambda - \lambda^{-2}\right)\left(C_1 + \lambda^{-1}C_2\right) \quad (2)$$

where C_1 and C_2 are constants characterizing the vulcanizates. However, Lawandy and Halim[14] showed that at strain values less than 16%, the parameter C_2 tends to be zero.

The same mixes used for stress–strain measurements were used to prepare other type of samples. These samples were subjected to various degrees of compressions. The compressed samples were subjected to ultrasonic waves.

It is known that the modulus of elastic material is defined as the ratio between stress and strain. This can be given by the relation:

$$E_y = F/A_0 \left(\frac{l - l_0}{l_0}\right)^{-1}$$
$$F/A_0 = E_y \left(\frac{l - l_0}{l_0}\right) \quad (3)$$

Relation between eqs. (1) and (3) can be expressed as follows

Figure 3 Stress–strain curves of rubber mixes containing TMTD and efficient vulcanizing systems.
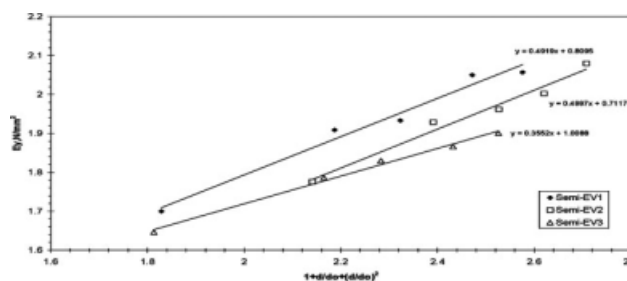

Figure 5 Relation between E_y and $1 + d/d_0 + (d/d_0)^2$ for mixes containing semi-efficient vulcanizing systems (semi-EV).
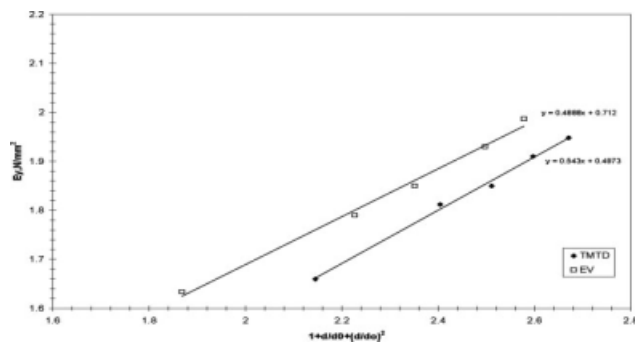
Figure 6 Relation between E_y and $1 + d/d_0 + (d/d_0)^2$ for mixes containing TMTD and efficient vulcanizing systems.

$$E_y \frac{(l - l_0)}{l_0} = \frac{\rho RT}{M_c}[l/l_0 - (l/l_0)^{-2}]$$

$$= \frac{\rho RT}{M_c}\left(\frac{l^3 - l_0^3}{l_0 l^2}\right)$$

$$E_y = \frac{\rho RT}{M_c}[l + l_0/l + (l_0/l)^2] \qquad (4)$$

The compression strain is a reversible process to that of elongation strain; and assuming that d_0 and d are the thickness of a sample before and after compression, respectively, relation (4) can be modified as:

$$E_y = \frac{\rho RT}{M_c}[1 + d/d_0 + (d/d_0)^2] \qquad (5)$$

Applying the elasticity terminals of the kinetic theory given in eq. (1) where the extension ratio, less than 16%, was expressed as $\lambda - \lambda^{-2}$ and the force applied expressed as F/A_0, $\lambda - \lambda^{-2}$ was plotted versus F/A_0. Consistent linear relations were obtained for the SBR rubber containing various curing systems. This can be shown in Figures 1–3. These curves showed different slopes depending on the vulcanizing system used in SBR rubber mixes. Substituting by the values of these slopes in eq. (1), the M_c was calculated; and subsequently, the crosslink density of the rubber mixes was obtained. The M_c
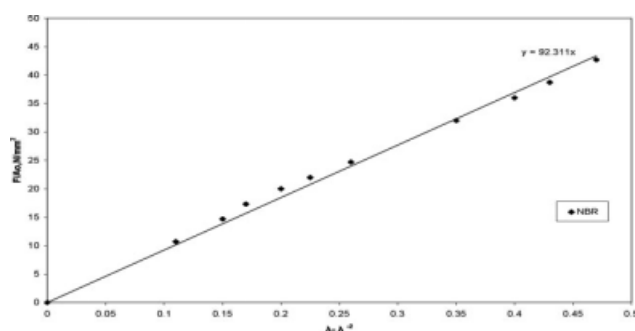

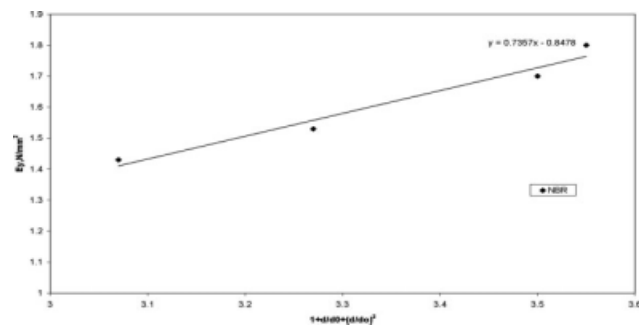**Figure 7** Stress–strain curves of NBR rubber mixes.

Figure 8 Relation between E_y and $1 + d/d_0 + (d/d_0)^2$ for NBR rubber mixes.

and crosslink density values for SBR vulcanizates are given can be shown in Table IV.

The Young's modulus, E_y, calculated from the ultrasonic measurements when plotted against the compression parameter $[1 + d/d_0 + (d/d_0)^2]$ linear relations were obtained. This can be shown in Figures 4–6. These curves showed once again various slopes depending on the curing system applied in the mix. Applying these slope values, the M_c values can be calculated using eq. (5) and subsequently the crosslink density of each rubber mix. The crosslink density values obtained from ultrasonic measurements are given in Table IV. From this table, one can notice that the crosslink density values obtained from stress–strain measurements and that obtained from ultrasonic measurements are in fair agreement.

To confirm the almost identical crosslink results obtained from both stress–strain and ultrasonic measurements for SBR rubber vulcanizates mixes; another polymer Butadiene-acrylonitrile (NBR) rubber based on another different mix was used to emphasize the use of ultrasonic technique in assessing the crosslink density of rubber. Figures 7 and 8 show the linear relationships obtained from the stress–strain and ultrasonic measurements, respectively. The slopes obtained were used to calculate the M_c and subsequently the crosslink density of the rubber mix. The M_c and crosslink density values are given in Table V. It is clear from the results that the ultrasonic technique is applicable also for NBR rubber mix.

As a result of this comparative study, the ultrasonic technique can be used successfully to calculate

TABLE V
M_c Values and Crosslink Density of NBR Rubber Vulcanizate

Technique	M_c value (g mole^{-1})	Crosslink density $\times 10^{-4}$ (g^{-1} mole)
Stress-Strain	3428	0.1458
Ultrasonic	3408	0.1467

the crosslink density of rubber vulcanizates as well as stress strain measurements.

CONCLUSIONS

The close agreement of average crosslink density estimated from both stress–strain measurements and that obtained from the ultrasonic technique makes the conception of applying the later technique a promising tool to evaluate many other microstructure parameters in the network rubber vulcanizates. It is a wide scope for future microstructure studies in this field.

References

1. Jacques, J. E. Rubber Technology and Manufacture, Published for the Institution of Rubber Industry; Buttworths: London, 1971.
2. Manik, S. P.; Banerjee, S. Angew Makromol Chem 1969, 6, 171.
3. Hassan, A. M.; Rav, L. N., Jr. J Appl Polym Sci 1971, 15, 145.
4. Spathis, G.; Kontou, E.; Saklabani, A. J Reinforced Plast Compos 1991, 10, 391.
5. Marzocca, A. J. J Appl Polym Sci 1995, 58, 1839.
6. Aprem, A. S.; Joesph, K.; Thomas, S. J Appl Polym Sci 2003, 91, 1068.
7. Marzocca, A. J.; Goyanes, S. J Appl Polym Sci 2003, 91, 2601.
8. Marzocca, A. J.; Mansilla, M. A. J Appl Polym Sci 2006, 103, 1105.
9. Vennemann, N.; Bökamp, K.; Bröker, D. Macromol Symp 2006, 245, 641.
10. Hergenrother, W. L. J Appl Polym Sci 1986, 32, 3027.
11. Youssef, M. H. Polymer 2001, 42, 10055.
12. Youssef, M. H. Polym Test 2003, 22, 235.
13. Higazy, A.; Afifi, H.; Khafagy, A.; El-Shahawy, M.; Mansour, A. Ultrasonic 2006, 44, e1439.
14. Lawandy, S. N.; Halim, S. F. J Appl Polym Sci 2005, 96, 2440.
15. Perepechko, I. Acoustic Method of Investigating Polymers, English Translation, Mir Publishers: Moscow, 1975.
16. Unnikrishnan, G.; Thomas, S. Polymer 1994, 35, 5504.
17. Varkey, J. T.; Augustine, S.; Groeninckx, G.; Bhagawan, S. S.; Rao, S. S.; Thomas, S. J Polym Sci Part B: Polym Phys 2000, 38, 2189.
18. Saville, B.; Watson, A. A. Rubber Chem Technol 1967, 40, 100.
19. Mooney, M. J Appl Polym Phys 1940, 11, 582.
20. Rivilin, R. S. Philos Trans R Soc 1948, A241, 379.
21. Mullins, L. J Appl Polym Sci 1959, 2, 1.
22. Rivilin, R. S.; Saunders, D. W. Trans R Soc 1951, 25, A243.