

Detection of Crosslink Density by Different Methods for Natural Rubber Blended with SBR and NBR

S. H. El-Sabbagh and A. A. Yehia,

Polymers and Pigments Department, National Research Centre,
Dokki, Cairo, Egypt

The crosslink density is an important property affecting the major characteristics of cured rubber. A comparison between the crosslink density calculations by different methods Rheometric, Swelling and Mooney-Rivlin methods for cured NR (natural rubber), SBR (styrene-butadiene rubber), NBR (nitrile rubber) and their blends were discussed. The obtained data by different comparison methods showed a very near results to each other. The best method among the three used methods for obtaining these results is the Mooney-Rivlin equation, due to its simple and reliable method for determination of crosslink density for cured rubber. Also, it is considered as an environmentally accepted method, since it depends on calculations and not using any hazardous solvents or chemicals.

1. Introduction:

Rubber is a class of polymeric materials, which is expected to show rubber elasticity when in use. Natural rubber is in use for its versatility as an elastomeric material. Synthetic rubbers, which appeared much later than natural rubber, now are commonly used, especially for pneumatic tires, after blending with other rubbers and carbon black as an effective reinforcing agent[1]. On the other hand, elastomer blends are widely used in rubber products for a variety of reasons, which include improved physical properties, improved service life, easier processing, and reduced production cost [2]. The blending of natural rubber (NR) with nitrile rubber (NBR) is intended to produce a vulcanizate with good oil resistant properties. Nitrile rubbers (NBR) have irregular chain structures i.e. amorphous; they do not crystallize when stretched.

Consequently, NBR is not self reinforced as NR and it requires a reinforcing filler or blending with other rubber to improve its mechanical properties. The main uses of NBR are in oil seals, and tubes [3-5]. Blends of NR

and SBR have been reported to exhibit improved oxidative stability compared to either pure components [5-10]. Elastomers are generally crosslinked in a random manner and therefore, it is difficult to identify the principal effects of modification through mixing of certain components on the mechanical properties [11]. The classical kinetic theory of rubber elasticity originally developed by Wall, Flory and James and Guth [12]. They attributed the high elasticity of a crosslinked rubber to the change of the conformational entropy of long flexible molecular chains. The theory predicts the following relation in simple extension

$$\sigma = A_{\phi} v_e K T (\lambda^2 - \lambda^{-1}) \dots\dots\dots(1)$$

Where σ is the true stress, the force per unit area measured in the strained state, v_e is the number of effective plastic chains per unit volume, K is Boltzman's constant, T the absolute temperature, and λ is the extension ratio; A_{ϕ} is a prefactor depending on the considered model. Zang et al [13] studied the elasticity of natural and SBR rubbers in simple extension at constant strain rate. They plotted the true stress as a function of $\lambda^2 - \lambda^{-1}$ as suggested by the molecular theory. They obtained a series of straight lines which do not pass through the origin.

Cross-linking in soft or flexible materials (rubber like) gives a considerable increase in elastic modulus, a marked increase in hardness, and usually a reduction in the ultimate elongation and permanent set [14]. The nature of cross-links plays a big role in determining the physical properties [14]. In other words, crosslink density is an extremely important factor in determining physical properties of a vulcanizate.

The objective of the present study is to compare crosslink densities for NR/SBR or NR/NBR blends determined by:

- (1) Stress-strain relation ship
- (2) Flory- Rehner equation⁽¹⁵⁾ of equilibrium volume swelling data Q .
- (3) By using rubber elasticity theory.

2. Materials and Techniques:

2.1. Material:

The rubbers used throughout this work are given in Table 1. The filler was high abrasion furnace carbon black (HAF), particle size 28 nm, and surface area about 65-70 m²/g. Other rubber ingredients were of grades customarily used in industry. All solvents and chemical reagents were of pure grade.

2.2. Techniques:

All rubber mixes were prepared on a laboratory two-roll mill of 470 mm. diameter and 300 mm. working distance. The speed of the slow roller was 24 r.p.m. with a gear ratio of 1:1.4. The rubber was mixed with ingredients according to ASTM (D15-72) and careful control of temperature, nip gap and sequenced addition of ingredients.

In this study natural rubber (NR) was blended with different ratios of styrene-butadiene rubber (SBR) as a non-polar and nitrile rubber (NBR) as a polar rubber. The ingredients mixed with the blends in phr: steric acid 1.5, ZnO 5, carbon black (HAF) 20, N-cyclohexyl-2-benzothiale sulfenamide (CBS) 1.25, isopropyl phenylenediamine (IPPD) 1 and sulfur 2.

Vulcanization was carried out in a single-daylight electrically heated auto controlled hydraulic press at $(152 \pm 1^\circ\text{C})$ and pressure 4MPa. The compounded rubber and vulcanizates were tested according to standard methods, namely:

- a) [ASTM D2084-95 (1994)] for determination of rheometric characteristics using a Monsanto Rheometer model 100.
- b) [ASTM D412-98a (1998)] for determination of physico-mechanical properties using Zwick tensile testing machine (model-1425).
- c) Fatigue properties were determined using a Monsanto Fatigue Failure Testing Machine, according to ASTM D 3629 (1998).
- d) Swelling was determined according to ASTM D 471-97(1998).

Table (1): Specifications of rubber types.

Name	Abbreviation	Type	Specific gravity	Mooney viscosity ML (1+4) at 100°C	Avg. molecular weight ^a	T _g °C
Natural Rubber	NR	Ribbed Smoked Sheets RSS-1	0.913 ± 0.005	60 – 90	174,189	-75
Nitrile Rubber	NBR	Butadiene acrylonitrile copolymer 32% acrylonitrile content	1.17 ± 0.005	45 ± 5	163,376	-45
Styrene-Butadiene Rubber	SBR	Butadiene/styrene copolymer styrene content ~ 23.5%	0.945 ± 0.005	52 ± 3	140,326	-60

^aCalculated in the previous work [7] using the Mark-Kuhn-Houwink equation.

Strain Energy Determination: Strain-energy values were obtained by plotting stress-strain curves for vulcanized rubber and the integrating area under the curves up to particular extension were used, to calculate the strain-energy, Simpson's rule ⁽¹⁶⁾ was applied. The calculated strain-energies were plotted against the corresponding strains. This curve was used to obtain the strain-energy for the particular extensions.

3. Results and Discussion:

The blends ratios together with the rheometric and physico-mechanical characteristics are given in Tables (2 & 3). From these data one can see clearly the increase of minimum torque M_L , maximum torque M_H , scorch time t_{s_2} (time to units of torque increase above minimum torque) and optimum cure time $t_{c_{90}}$ (the time to 90% of maximum torque) as SBR or NBR content increases in the blend, while the cure rate index (CRI) is decreased in these blends. This can be attributed to the nature of NR, SBR and NBR gum rubbers, since NR vulcanizes faster than both SBR and NBR. This is based on the fact that, the degree of unsaturation of NR is greater than that of both SBR and NBR, which contain some segments of styrene and acrylonitrile. It is worthy to mention that the mechanical properties of NR vulcanizates is higher than that of both of SBR and NBR, since NR is crystalline when stretched and the others are amorphous. Determination of crosslink density via rheometric data.

Table (2): NR/SBR blend composition with the rheometric and physico-mechanical characteristics.

Ingredient in phr / Formulation No	S ₁	S ₂	S ₃	S ₄	S ₅
NR	100	75	50	25	- - -
SBR	- - -	25	50	75	100
Rheometric characteristic at 152 ± 1°C					
M_L , dN.m	2.00	2.50	3.75	6.00	9.00
M_H , dN.m	56.00	58.00	60.50	64.00	66.00
ΔM , dN.m	54.00	55.50	57.00	58.0	57.00
T_{s_2} , min.	2.75	3.00	3.50	4.50	5.00
$T_{c_{90}}$, min.	8.50	10.00	13.00	17.00	21.00
CRI, min. ⁻¹	17.39	14.28	10.53	8.00	6.25
The physical properties of NR/SBR blend vulcanizates at optimum cure time					
Modulus at 100% strain, MPa	2.44	2.64	2.71	2.89	2.92
Modulus at 200% strain, MPa	4.28	4.31	4.42	4.5	4.58
Tensile strength, MPa	21.80	18.82	16.90	14.85	12.75
Strain at break, %	797	695	625	550	495
Young's modulus, N/mm ²	0.278	0.310	0.354	0.365	0.379
No. cycles until fracture (fatigue)	19624	18720	17425	16982	16325

Table (3): NR/NBR blend composition with the rheometric and physico-mechanical characteristics.

Ingredient in phr /F formulation N	S ₁	S ₆	S ₇	S ₈	S ₉
NR	100	75	50	25	- - -
NBR	- - -	25	50	75	100
Rheometric characteristic at 152 ± 1°C					
M _L ,dN.m	2.00	3.00	4.00	4.75	7.75
M _H ,dN.m	56.00	60.00	64.00	69.00	71.00
Δ M , dN.m	54.00	57.00	60.00	64.25	63.25
Ts ₂ , min.	2.75	3.00	3.25	3.50	4.50
Tc ₉₀ ,min.	8.50	9.50	11.00	13.00	15.00
CRI , min. ⁻¹	17.39	15.38	12.9	10.53	9.53
The physical properties of NR/NBR blend vulcanizates at optimum cure time					
Modulus at 100% strain ,MPa	2.44	2.61	2.73	2.88	2.97
Modulus at 200% strain, MPa	4.278	4.39	4.82	5.01	5.58
Tensile strength ,MPa	21.80	21.00	20.20	18.60	18.33
Strain at break, %	797	780	690	615	610
Young's modulus, N/mm ²	0.278	0.480	0.635	0.700	0.925
No. cycles until fracture (fatigue)	19624	19031	15000	13345	11200

It is known that the torque difference can be indirectly related to the crosslink density of the blends [2]. Consequently the degree of crosslinking [17] in the rubber blends was determined using the rheometric data. It was found that the difference between maximum and minimum torques Δ M increases in NR/ SBR and NR/ NBR blends as the content of NR decreases in the blend. The relationship between the torque difference (Δ M) and the content of NR is shown in Fig. (1). This figure clearly shows that NR/ SBR blend is more compatible blend than NR/ NBR blend. The decreasing torque difference for NR/ SBR or NR/NBR blends indicates that the crosslink densities decrease as NR increases in the blend. Therefore ΔM can be taken as the extent of crosslink density in the rubber phase [18].

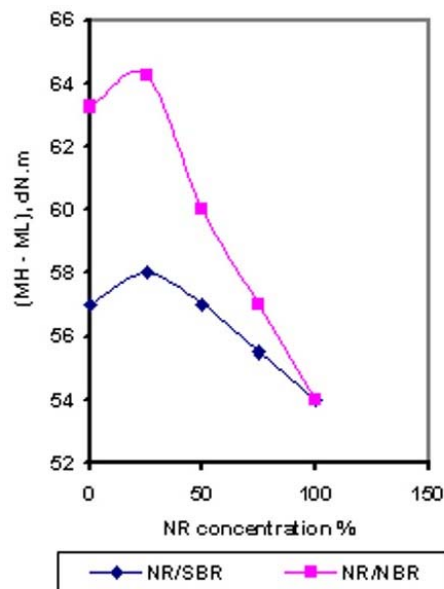


Figure 1: Variation of torque value ($M_H - M_L$) with % concentration of NR for NR/SBR and NR/NBR

The above findings can be confirmed by the modulus at 100 and 200% strain data, which are given in Tables (2 & 3). These parameters decrease as the content of NR increases in the blend. The calculated Young's modulus (elastic modulus) is determined from the slope of the relation between the stress and strain as shown in Fig. (2a & b) is an additional proof to this conclusion. The higher tensile strength and fatigue life of NR vulcanizates than both for NBR and SBR can be due crystallinity of NR and amorphous state of NBR and SBR gum rubbers.

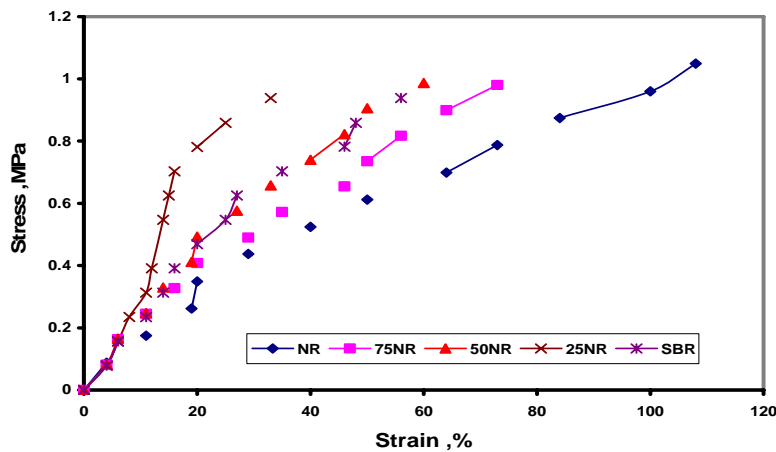


Figure 2a: Stress-Strain curves for NR/SBR blends

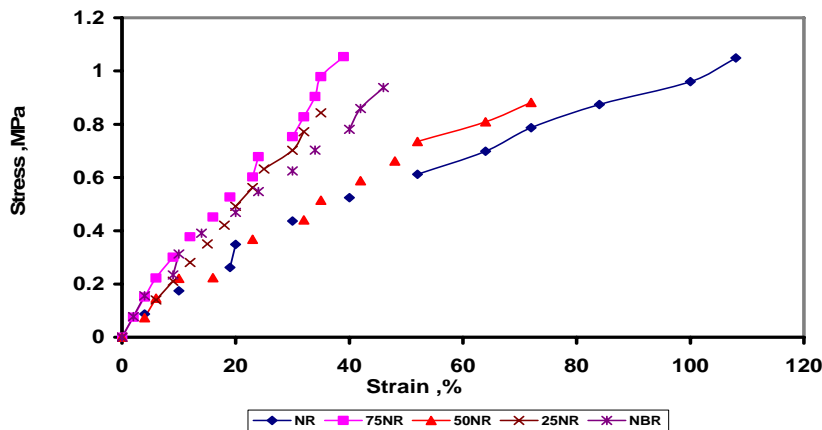


Figure 2b : Stress-Strain curves for NR/NBR blends

Determination of crosslinking using Mooney-Rivlin equation:

The stress-strain curves of the NR/ SBR and NR/ NBR blend are shown in Fig. (2a & b). It has been shown by Rivilin *et al.* [19] that the stress-strain behavior of rubber vulcanizates can be described by the Mooney-Rivlin relation which in simple extension, gives:

$$\sigma = 2(C_1 + C_2/\alpha)(\alpha - 1/\alpha^2) \tag{2}$$

where σ is the true stress, which produce an extension ratio in the sample, α is the strain ratio and C_1 and C_2 are parameters characteristics of the rubber vulcanizates. It has been shown that, C_1 is a quantity pertaining the ideal elastic behavior, while C_2 express the departure from the ideal elastic behavior tensile results are displayed in the from of the Mooney-Rivlin simple were evaluated and plot in Fig. (3a, 3b). The Stress-Strain curves of Fig.(3a) are re-plotted with the use of the variable strain-amplification factor. Constants C_1 and C_2 have been obtained with the use of the strain amplification factor X, which is defined as:

$$X = \sigma / \varepsilon E_0 = E / E_0 \tag{3}$$

where ε is the strain produced by a stress σ , and E_0 is the modulus of the matrix, which means that the local strains are on the average X times is greater than the overall strains. So, the extension ratio α in Eqn. (2) is replaced by $\Lambda = 1 + X \varepsilon$. Knowing the strain amplification factor given by Eqn. (3), the curves of Fig. (3a & b) are re-plotted in Fig. (4a & b). From Fig. (4), the constant C_1 and C_2 are readily determined, and their dependence on the concentration of the blends and kinetic theory of rubber elasticity is given by :

$$2 C_1 = \nu KT \tag{4}$$

where, K is the Boltzmann's constant and T is the absolute temperature. The constant C_1 is related to the network-chain density ν in Eqn. (4). From the linearity in re-plotted Fig. 3, C_1 , C_2 and then ν were calculated for NR/SBR, NR/ NBR blends and listed in Table (4). It is clearly seen that, the crosslink density (ν) was decreased by increasing NR in the NR/SBR or NR/ NBR blends.

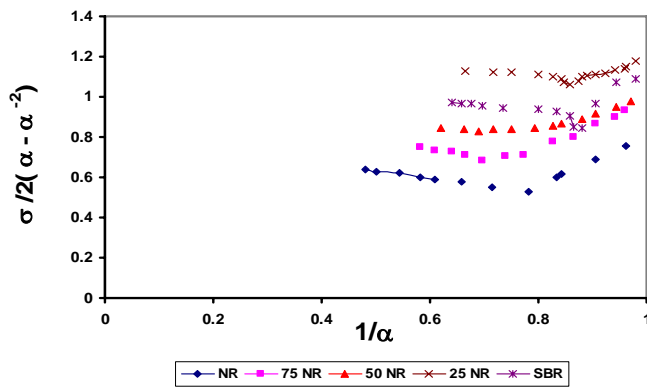


Figure 3a : The Mooney-Rivlin plots for NR/SBR blends

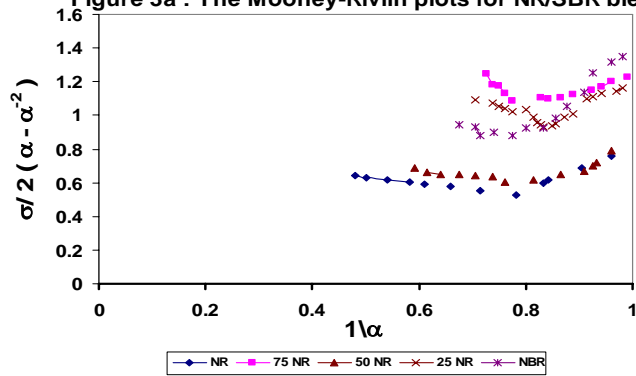


Figure 3b : The Mooney-Rivlin plots for NR/NBR blends

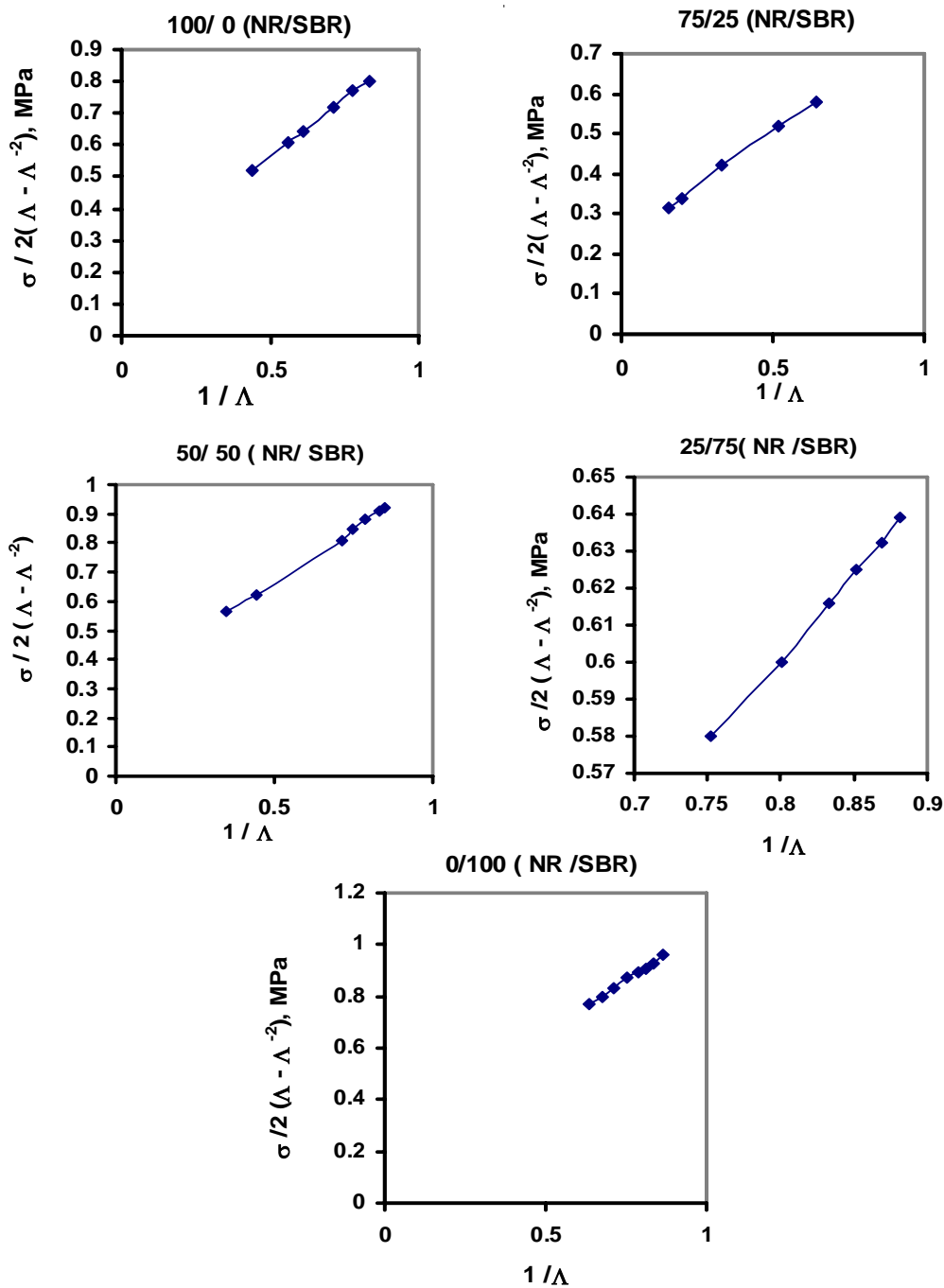


Fig. 4a: Stress-Strain curves of NR/SBR blends of Fig.3a re-plotted with the use of the variable strain-amplification factor

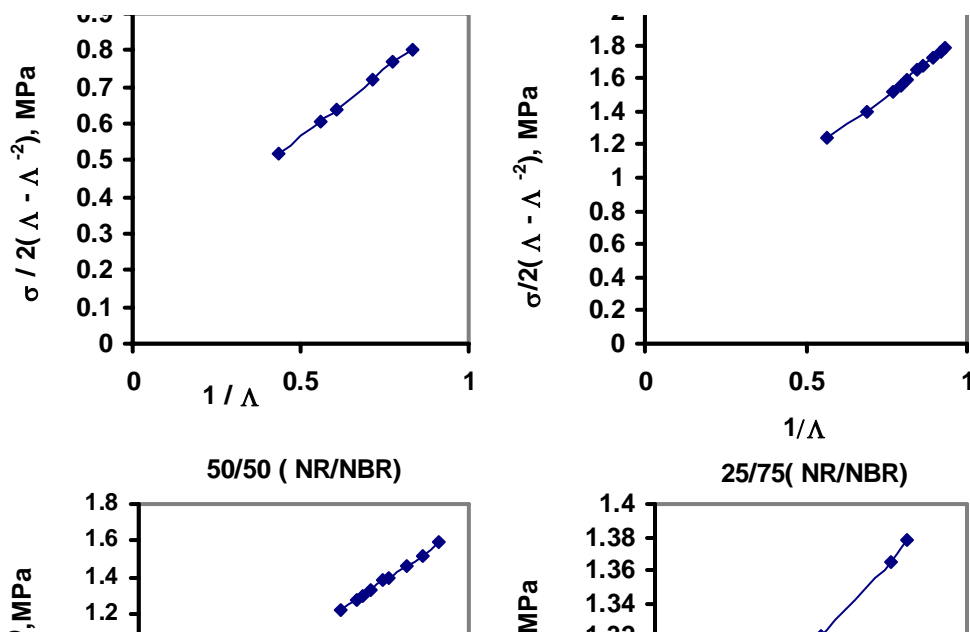


Figure 4b: Stress-Strain curves of NR/NBR of Fig.3b re-plotted with the use of the variable strain-amplification factor

Sample No.	C ₁ ,MPa	C ₂ ,MPa	v x 10 ⁴ (mole/cm
S ₁ (NR)	0.2300	0.6990	1.860
S ₂ 75/25(NR/SBR)	0.2535	0.5347	2.048
S ₃ 50/50 (NR/SBR)	0.2826	0.7898	2.284
S ₄ 25/75 (NR/SBR)	0.2928	0.4019	2.366
S ₅ (SBR)	0.3021	0.7519	2.440
S ₆ 75/25(NR/NBR)	0.3638	1.4124	2.939
S ₇ 50/50 (NR/NBR)	0.4610	1.4464	3.725
S ₈ 25/75 (NR/NBR)	0.5323	1.4803	4.302
S ₉ (NBR)	0.5841	1.8723	4.720

Determination of crosslink density using swelling data:

Linear polymers often will completely dissolve in their own monomers or in another good solvent⁽²⁰⁾. A good solvent for a polymer is one that is either similar in chemical structure to the polymer or one, which can interact with the polymer main-chain or side groups.

One way for determining the solubility of polymers in solvent is through the estimation of solubility parameter (δ). The following relationship can often be used to estimate the solubility of a polymer in a solvent^(21, 22).

$$\text{i.e.; if } (\delta_1 - \delta_2)^{1/2} < 1 \quad (4)$$

then the polymer will dissolve in the solvent. Using a group contribution analysis approach, the solubility parameter of a material can be estimated by the following equation⁽²⁰⁾.

$$\delta = (\rho \sum F_i) / M \quad (5)$$

where δ = the solubility parameter, ρ = the density of the material; F_i = the group molar attraction constant; M = the molecular weight of the material. Using Eqn. (4), we find the square-root of the difference between rubber and solvent (Toluene) as shown in Table (5):

Table (5): The values of solubility parameter of the rubber under investigation

	$(\delta_1) (\text{ cal/cc})^{1/2}$ for rubber	$(\delta_2) (\text{ cal/cc})^{1/2}$ for solvent	$(\delta_1 - \delta_2)^{1/2} (\text{ cal/cc})^{1/2}$
NR	8.1	8.9	0.89
SBR	8.04	8.9	0.927
NBR	9.25	8.9	0.59

From the previous results, it can be concluded that toluene is a good solvent for the three rubbers (NR, SBR & NBR). Therefore; toluene is the most suitable solvent.

The swelling of a rubber by a liquid is a mixing process; two substances mix when the free energy of mixing (ΔG) is negative, if the change in enthalpy (ΔH) is less than the product of absolute temperature (T) and the change in entropy ΔS as given by the Gibbs equation:

$$\Delta G = \Delta H - T \Delta S \quad (6)$$

In simple terms, mixing is favored by minimum or negative enthalpy change and mixing entropy change [23].

Equilibrium swelling in toluene was used to determine the crosslink density of the different blend ratios. Consequently, it was possible to make use of the swelling data to calculate the molecular weight between two successive crosslinks (M_c) by the application of the well known Flory Rehner equation [15].

$$1/M_c = -1/2\rho V_0 [(\ln(1 - V_R) + V_R + \mu V_R^2) / (V_R^{1/3} - 1/2 V_R)] \quad (7)$$

and hence the crosslink density can be calculated from the equation

$$\text{Crosslink density } (\nu) = 1/2M_c \quad (8)$$

Where ρ is the density of rubber; V_0 is the molar volume of solvent absorbed (toluene $V_0=106.3 \text{ cm}^3/\text{mole}$); V_R is the volume fraction of the rubber in the swollen material.

The equilibrium swelling measurements, soluble fractions, molecular mass (M_c) and the crosslink density ν were calculated and listed in Table (6). One can notice that, equilibrium swelling and M_c were decreased, while the soluble fraction and crosslink density ν increased by increasing either SBR or NBR content in the blends.

This may be attributed to the different nature of the two rubbers. In the other words the crystallinity of NR, the polarity of NBR ($C \equiv N$) and non

polarity of SBR play a definite role in this directions. The obtained data are in good agreement with the previous result.

On the other hand, rubber elasticity theory predicts that the relation between the tensile strength and the elongation ratio⁽²⁴⁾, λ , is;

$$\sigma = \sigma_0(\lambda) + E (\lambda^2 - 1/\lambda) \tag{9}$$

where σ is the stress, E is the modulus of elasticity and λ is the extension ratio. Figure (5a & b) illustrate the relation between $(\lambda^2 - 1/\lambda)$ and stress (σ) for NR/SBR and NR/NBR blends. From these figures, it has been calculated the slope of these lines, and then tried to calculate the average molecular weight M_c between crosslinks from the value G according to the well known relation [12]:

$$G = 3E = A_\phi \rho RT/M_c \tag{10}$$

where G shear modulus, ρ is the density of the rubber and R the gas constant, The value of M_c can be calculated and hence the crosslink density ν . The obtained data are listed in Table 5 for NR/SBR and NR/NBR blends assuming $A_\phi = 1$ (A_ϕ is the front factor) [25]. It can be see that the values of crosslink density ν are relatively close to the previous values, which were calculated by the other two different methods (Table 4 & 6). It should be noticed that the value of crosslink density ν is higher for NR/NBR blend than for NR/SBR blend this due to the chemical nature of the considered rubber. This is in agreement with the relation between strain energy versus blend ratios of NR/SBR or NR/NBR blends (Figure 6). One can see that strain energy of NR/SBR blend vulcanizates have linear behavior of decreasing gradient between NR and SBR. While nonlinear relationship of NR/NBR can be attributed to the incompatibility of NR and NBR.

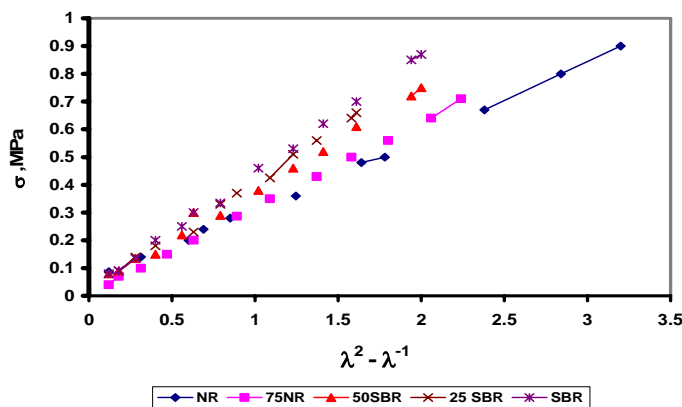


Figure 5a: Stress as a function of $\lambda^2 - \lambda^{-1}$ for NR/SBR blend

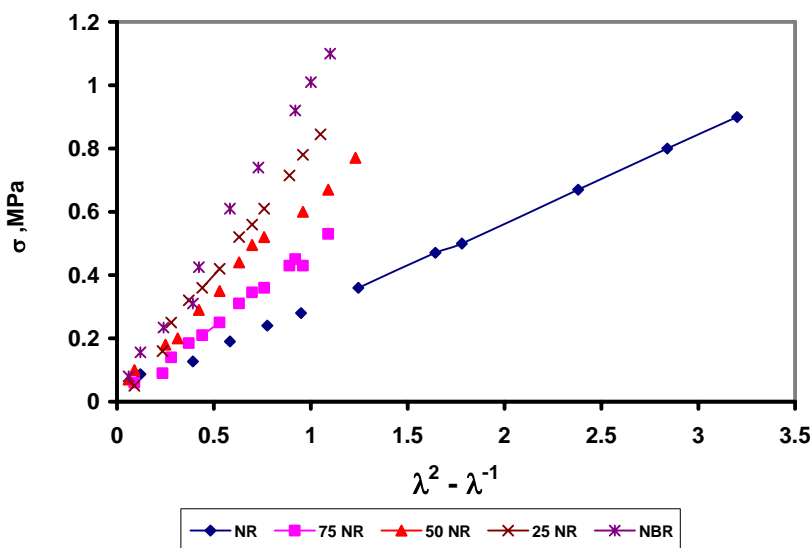


Figure 5b: The stress as function of $\lambda^2 - \lambda^{-1}$ for NR/NBR blends

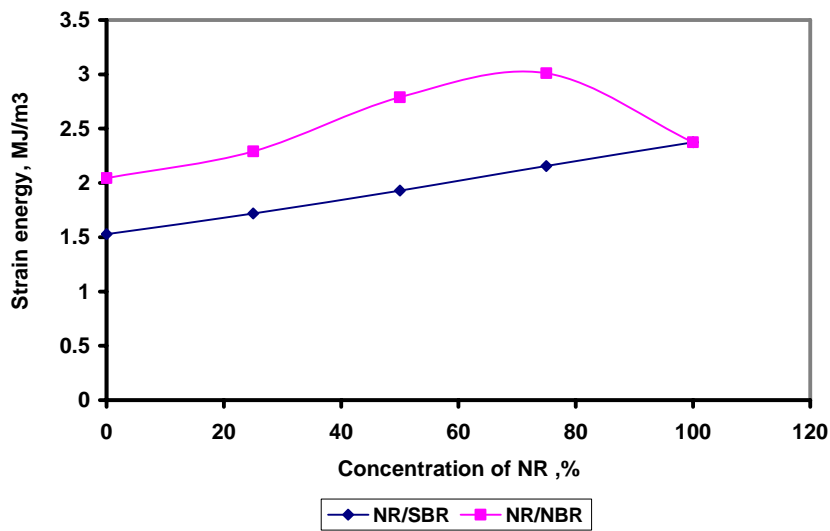


Figure 6: The variation of strain energy versus the blend ratio for NR/SBR and NR/NBR blends

Table (6): Swelling characteristics for NR/SBR and NR/NBR rubber blends

Sample No.	Equilibrium swelling Q (%)	Soluble Fraction (%)	M. weight bet. Crosslinks Mc (g/mole)	$\nu \times 10^4$ (mole/cc)
S ₁ (NR)	252	4.2	2675	1.870
S ₂ 75/25(NR/SBR)	230	4.9	2436	2.053
S ₃ 50/50 (NR/SBR)	208	5.3	2184	2.289
S ₄ 25/75 (NR/SBR)	198	6.0	2133	2.344
S ₅ (SBR)	186	7.0	2026	2.460
S ₆ 75/25(NR/NBR)	201	4.0	1695	2.949
S ₇ 50/50 (NR/NBR)	158	3.8	1348	3.710
S ₈ 25/75 (NR/NBR)	140	3.2	1162	4.304
S ₉ (NBR)	128	2.7	1056	4.737

Table (7): The value of G, Mc and crosslink density ν for NR/SBR and NR/NBR blends

Sample No.	G (MPa)	Mc (g/mole)	$\nu \times 10^4$ (mole/cm ³)
S ₁ (NR)	0.840	2693	1.856
S ₂ 75/25(NR/SBR)	0.930	2450	2.04
S ₃ 50/50 (NR/SBR)	1.053	2180	2.293
S ₄ 25/75 (NR/SBR)	1.089	2123	2.35
S ₅ (SBR)	1.155	2016	2.48
S ₆ 75/25(NR/NBR)	1.422	1703	2.939
S ₇ 50/50 (NR/NBR)	1.890	1365	3.662
S ₈ 25/75 (NR/NBR)	2.355	1163	4.297
S ₉ (NBR)	2.760	1050	4.76

This is due to the relatively weak interaction at the boundary areas of the phases NR and NBR, which causes the overlap between the curves of NR/NBR blend.

By using the above equations to calculate the crosslink density have the advantages in reducing the use of solvents and thus avoid the pollution of the environment.

Conclusions:

It can be concluded that's tress at 100 or 200% strain and Young's modulus are increased by increasing NBR or SBR in the blend, while tensile strength, strain at break and fatigue life are decreased. Equilibrium stress-strain measurements were carried out using Moony-Rivlin relation, which was used to deduce the constants, also the cross-linking density ν was calculated. This relation compensates the usage of solvents and this is environmentally needed. The value of crosslinking density ν for NR/NBR blend was higher than the value of ν for NR/SBR, this may be due to the nature of the used rubber. The value of strain energy for NR/NBR blends was higher than for NR/SBR blends depending on their compatibility. A good agreement was found between the crosslinking density ν obtained by shear modulus (G) measurement and that obtained by other methods such as solvent swelling or tensile stress-strain measurement for NR/SBR and NR/NBR blends. The rheometric measurements demonstrated the degree of cross-linking in the rubber compounds.

References

1. S. Kohjya; *Rubber Chem. and Technol.*, **73**(3), 534 (2000).
2. H. Ismail, S. Tan and B. Tpo.; *J. of Elastomers and Plastics*, **33**, 251 (2001).
3. S. H. El-Sabbagh, A. I. Hussain and M. A. Abd El-Ghaffar; *Pigment & Resin Technology*, **34**(4), 203 (2005).
4. M.N. Ismail, S. H. El-Sabbagh, A. A. Yehia, *J. Elastomers and Plastics*, **31**, 255 (1999).
5. A. L. G. Saad, S. H. El-Sabbagh; *J. Applied Polymer Science*, **79**, 60 (2001).
6. S. H. El-Sabbagh; *Polymer Testing*, **22**, 93 (2003).
7. A. A. Yehia, F. M. Helaly and S. H. El-Sabbagh; *Advances in Polymer Blends and Alloys Technology*, **4**, 102 (1993).
8. A. A. Yehia, A. A. Mansour and B. Stoll; *J. Thermal Analysis*, **48**, 1299 (1997).
9. M. J. Folkes and P. S. Hope, "Polymer Blends and Alloys". Blackie Academic & Professional an imprint of Chapman & Hall, p.66 (1993).
10. S. H. El-Sabbagh, A. I. Hussein and M. A. Abd El- Ghaffar, *Pigment & Resin Technology*, **34** (4), 203 (2005).
11. M. S. Sobhy; *Polymer International*, **42**, 85 (1997).
12. L. R. G. Treloar, "The Physics of Rubber Elasticity", 3rd., Oxford Univ. Press (1975).
13. Y. H. Zang, R. Muller and D. Froelich; *Journal Rheology*, **30** (6), 1165 (1986).
14. S. Lee and H. Pawlowski, *Rubber Chem. & Technol.*, **67**, 854 (1994).
15. C. R. Parks; *J. Rubber Chem. And Technol.*, **55**, 1170 (1982).

16. D. Honiball and W. J. Mc Gill, *J. Polym. Sci., B. Polymer Physics*, **26**, 1529 (1988).
17. R. S. Rivlin and A. G. Thomas; *J. Polym.Sci.*, **10**, 291 (1953).
18. M. Arroyo, M. A. Lo`pez-Manchado and B. Herrero; *Polymer*, **44**, 2447 (2003).
19. K. Ajay Manna , P. P. De, D. K. Tripathy, S. K. De and M. K. Chatterjee; *Rubber Chem. & Technol.*, **72** (2), 398 (1999).
20. L. Mullins, N. R. Tobin, *J. Appl. Polym. Sci.*, A: 2993 (1965).
21. N. G. Mc Crum., C.P. Buckley and C. B. Bucknall, "*Principles of Polymer Engineering (2nd Edition)*", *Oxford Science Publications*, pp.100-111 (1997).
22. L. H. Sperling, "*Polymeric Multicomponent Materials*", John Wiley & Sons, Inc., pp.62-67 (1997).
23. M. F. Myntti and N. Laboratories; *Rubber World*, **228** (3), 38 (2003).
24. H. Philip Starmer ; *J. Elastomers and Plastics*, **25** (3), 188 (1993).
25. M. I. Aranguren; E. Mora; C. W. Macosko and John Saam; *Rubber Chem. & Technol.*, **5**, 820 (1994).
26. A. Sharaf; *Rubber Chem. & Technol.*, **67**, 88 (1994).