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DETERMINATION OF CROSSLINK CONCENTRATION BY MOONEY-RIVLIN EQUATION FOR VULCANIZED NR/SBR BLEND AND ITS INFLUENCE ON MECHANICAL PROPERTIES

(Menentukan Kepekatan Hubung Silang Menggunakan Persamaan Mooney-Rivlin untuk Campuran Getah Tervulkan NR/SBR dan Pengaruhnya Terhadap Sifat Mekanikal)

Azreen Izzati Dzulkifli*, Che Mohd Som Said, Chan Chin Han

Faculty of Applied Sciences,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

**Corresponding author: izzati_dzulana@yahoo.com*

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Abstract

Crosslink concentration is an important property affecting the major characteristic of cured rubber. The crosslink concentration was determined using Mooney-Rivlin equation due to its simple and reliable method. Cured natural rubber and styrene butadiene rubber blend (NR/SBR) with different crosslink concentrations were obtained with different blend ratios of 100/0, 80/20, 70/30, 60/40, 50/50, 40/60 and 0/100. The crosslink concentrations were determined using Mooney-Rivlin Equation and its influence on International Rubber Hardness Tester (IRHD), tensile strength and rebound resilience of NR/SBR blend vulcanizates was investigated. The results showed different blend ratios had an influence on the crosslink concentration of the NR/SBR blend vulcanizates. Obtained data showed that high NR content in NR/SBR blend increased the crosslink concentration. The highest crosslink concentration recorded was for 100/0 blend ratio which was 0.0498 mol kg^{-1} RH while the lowest was 0.0295 mol kg^{-1} RH for 0/100 blend ratio. The study on the influence of crosslink concentration on IRHD, tensile strength and rebound resilience of NR/SBR blend vulcanizates showed that the mechanical properties increased linearly with the crosslink concentration. High NR content in NR/SBR blends resulted in higher crosslink concentration which improved the performance of mechanical properties for NR/SBR blend.

Keywords: crosslink concentration, Mooney-Rivlin equation, natural rubber, styrene butadiene rubber

Abstrak

Kepekatan hubung silang adalah perkara penting yang mempengaruhi ciri-ciri utama getah tervulkan. Kepekatan hubung silang telah ditentukan dengan menggunakan persamaan Mooney-Rivlin kerana ia merupakan kaedah yang mudah dan telah diperakui. Campuran getah asli dan stirena butadiena (NR/SBR) dengan kepekatan hubung silang yang berbeza telah diperolehi oleh penggunaan nisbah campuran yang berbeza iaitu 100/0, 80/20, 70/30, 60/40, 50/50, 40/60 dan 0 / 100. Kepekatan hubung silang telah ditentukan menggunakan persamaan Mooney-Rivlin dan pengaruhnya ke atas Ujian Kekerasan Getah Antarabangsa (IRHD), kekuatan tegangan dan pemulihan daya tahan campuran getah NR/SBR telah dikaji. Hasil kajian menunjukkan nisbah campuran yang berbeza mempengaruhi kepekatan hubung silang getah tervulkan NR/SBR. Data yang diperolehi menunjukkan bahawa kandungan getah asli (NR) yang tinggi dalam campuran NR / SBR memberikan peningkatan terhadap kepekatan hubung silang. Kepekatan hubung silang tertinggi dicatatkan adalah untuk nisbah campuran 100/0 iaitu 0.0498 mol kg^{-1} RH, manakala yang terendah adalah 0.0295 mol kg^{-1} RH untuk nisbah campuran 0/100. Kajian ke atas pengaruh kepekatan hubung silang terhadap ujian IRHD, kekuatan tegangan dan pemulihan daya tahan campuran getah masak NR/SBR menunjukkan bahawa sifat-sifat mekanikal meningkat secara selari dengan kepekatan hubung silang. Kandungan getah asli (NR) yang tinggi dalam campuran getah NR/SBR menyebabkan kepekatan hubung silang yang lebih tinggi dan sekaligus meningkatkan prestasi sifat mekanik campuran getah NR/SBR.

Kata kunci: kepekatan hubung silang, persamaan Mooney Rivlin, getah asli, getah stirena butadiena

Introduction

Rubber is a polymeric material which has elasticity behaviour when in used [1]. It is important to know that rubber do not display all of the characteristics that are required for that specific application. Thus, rubber blends were introduced and widely used in rubber products for a variety of reasons. Studies on natural rubber (NR) were done extensively because of the superior performance reported in the tire applications [1]. So, there were many studies on NR and its blend compounds.

The blending of two or more rubbers is a useful technique to improve certain properties and developing materials with properties superior to those of individual constituents. Blends of NR have been widely studied and were reported to have a good compatibility that resulted in providing desirable mechanical properties [2]. NR with high percent of cis- 1, 4 structure has stronger tensile strength than synthetic rubbers because of the crystallization produce by the orientation. It can be concluded that natural rubber can be blended with synthetic rubbers in order to improve their mechanical properties such as tensile strength, resilience, tear strength, fatigue, fracture or etc. [3]. The purpose of blending natural rubber (NR) and styrene butadiene rubber (SBR) during the production of rubber products are to lower the compounding cost and also for easily fabricated of complex shaped product [2]. According to Azemi Samsuri [4], SBR offers better abrasion resistance than NR. Thus it gives a wide application for SBR to be used in tire manufacturing. Relatively high T_g of SBR was the factor for the high heat generation as the tires were deformed dynamically when the vehicle was moving, so it is usually to blend SBR with low T_g rubbers like NR to minimize the risk of blowout failure.

L. Bohn studies on the compatibility of different polymer blend reported that the extent of blend homogeneity and compatibility were depending on the mixing method, solubility parameters and the nature of blends constituent rubbers [3]. NR/ SBR blend showed relatively good homogeneity that favoured by rather similar solubility parameter which is 16.7 $MPa^{1/2}$ for NR while 17.5 $MPa^{1/2}$ for SBR. The closer the solubility parameter, the better was their compatibility. In this research, differential scanning calorimetry (DSC) was used to study the compatibility between SMR-L/SBR rubber blends by evaluating the glass transition temperature, T_g values.

The physical properties and mechanical strength such as tensile strength tear strength, hardness, resilience of vulcanized rubber and many others were known to be affected by crosslink concentration [4]. The nature of crosslinking plays a big function in determining the physical properties. In other words, crosslink density is an important factor in determining physical properties of a vulcanizate. Thus, it is very important to determine or measure quantitatively the crosslink concentration of the vulcanized rubber. Crosslinking in rubber like materials give a considerable increase in elastic modulus, a marked increase in hardness, and usually a reduction in the ultimate elongation [1].

There are two common methods to determine the crosslink concentration of vulcanized rubber network. First, means of equilibrium swelling measurement and second by simple extension measurement [5]. In this study, seven NR/SBR formulations of different blend ratios were compound and the crosslink concentrations were determined by simple extension measurement method due to its simple and reliable method. It is considered as an environmentally accepted method since it depends on calculation and not using any hazardous solvents [1]. Mechanical properties were studied by tensile, hardness and resilience test.

The objectives of this research were to determine the crosslink concentration for vulcanized NR/ SBR blend at various blend ratios and investigating the effect of crosslink concentration on mechanical properties of vulcanized rubber blend based on tensile, hardness and resilience test.

Materials and Methods

Materials and Preparation of Rubber Blend Compound

The materials used in this study were SMR-L type of natural rubber and SBR-1502 type of styrene butadiene rubber supplied by Rubber Research Institute of Malaysia (RRIM). Their descriptions are shown in Table 1. Seven rubber compounds were prepared in different blend ratios by keeping fixed the total rubber quantity specified in the standard testing recipe. The compounding recipes of SMR-L/SBR-1502 blends are shown in Table 2.

Table 1. Specifications of rubber types

Name	**Abbreviation**	**Type**	**Supplier**
Natural Rubber	NR	SMR-L (Standard Malaysia Rubber-Light)	Rubber Research Institute of Malaysia (RRIM)
Styrene Butadiene Rubber	SBR	SMR-1502	Rubber Research Institute of Malaysia (RRIM)

The rubber was mixed with ingredients using 2-roll mill machine and careful control of the temperature, nip gap and sequenced addition of ingredients are very important. Curing characteristic of SMR-L/SBR blends was studied using Mosanto Rheometer according to ISO 3417. Samples of about 10 g of each blend were used to test at 150 °C. The blends then were compression moulded at 150 °C according to respective cure time obtained from the rheometer. Then the required samples for mechanical tests were prepared.

Table 2. Rubber formulation for SMR-L/SBR-1502 blends compound

Ingredients (PHR)	**No. of Compounds**						
	1	**2**	**3**	**4**	**5**	**6**	**7**
SMR-L/SBR-1502	100/0	80/20	70/30	60/40	50/50	40/60	0/100
ZnO	5	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2	2
TMQ	2	2	2	2	2	2	2
CBS	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Crosslink Concentration Measurements

The test piece was a long parallel strip with a uniform thickness of vulcanized rubber which about 120 mm x 3.2 mm x 1 mm. Two end of the test piece were clamped tight enough to avoid slippage by the clamps attached to C_1 machine as shown in Figure 1. After zeroing the force by pressing the tare button, the test piece was pulled at various pre-determined extensions. At each extension, the force can only be recorded after 3 minutes. Then the test piece was pulled to the next pre-determined extension and the force was recorded 3 minutes later. This same sequence was repeated until at least twelve readings were obtained and the elastic constant C_1 can be determined from the Mooney-Rivlin Equation [4].

$$f/\left[2A_o\left(\lambda-\lambda^{-2}\right)\right]=C_1+C_2\lambda^{-1} \quad (1)$$

where f was the force, A_0 was cross-sectional area (unstrained state), and λ was the extension ratio. By plotting $f/[2A_0(\lambda-\lambda^{-2})]$ vs λ^{-1} the value of C_1 was obtained as the intercept of the graph. The elastic constant C_1 is related to the physically manifested crosslink concentration, $[X]_{phy}$ by the mathematical relation given in equation 2 below

$$C_1 = \rho RT\,[X]_{phy} \tag{2}$$

Figure 1. C_1/Stress relaxation machine

Measurement of Mechanical Properties

The tensile properties of the blends were measured using an Instron 5569 Tensile Machine, according to ISO 37 standard. The crosshead speed for the tensile test was set at 500 mm/min. All test was perform at room temperature (25 ± 2° C). Specimens prepared for the tensile test were in dumbbell shape and a total of five samples from each formulation were tested [4].

The hardness measurements were performed according to ISO 48 standard by an International Rubber Hardness Tester (IRHD) and a cylindrical specimen was required for the test. Pressure foot were applied to the test pieces and readings were taken within 30 seconds specified time after applying the indenting force. Minimum 5 measurements were taken and average values were reported [4].

Rebound resilience test was done by using Dunlop Tripsometer according to ISO 4662 and a cylindrical specimen was required. The test piece thickness should be adequately thick with 12 mm. Two test pieces were tested. The pendulum was released from vertical position (45°) to strike the test piece. Three rebound readings were noted by the machine. The median values were taken as the rebound resilience of the test piece [4].

Differential Scanning Calorimeter (DSC) Measurement

Thermal analysis using DSC measurement of each cured rubber blend samples were performed with NETZSCH DSC 200 F3 instrument. Samples of about 10 mg were initially cooled under nitrogen atmosphere from ambient temperature to -80 °C and then heated to 25° C at a rate of 10° C/min. Obtained results were used to evaluate the glass transition temperature, T_g in order to study the compatibility of rubber blends.

Results and Discussion

Cure Characteristics

It is very important to vulcanize the rubber compound to its optimum state of cure in order to obtain well balances physical properties. The optimum cure time was defined as the time required producing optimum physical properties for the vulcanized rubber. In order to obtain the optimum state of cure, the rubber compound was vulcanized to 95% of its maximum state of cure. All the rheometric characteristics for every blend ratios were stated in Table 3. From these data, it can be seen clearly the increase of scorch time ts_2 and the optimum cure time, t_{95} as SBR content increase in the blend, while the cure rate index, (CRI) was decreased in these blends. It was attributed to the nature of SMR-L that has greater degree of un-saturation than SBR, which contain some segments of styrene. Thus, it gave faster vulcanization of SMR-L than SBR.

Table 3. Rheometric characteristics for every vulcanized rubber blend ratios

	Blend ratio						
(SMR-L/SBR)	**100/0**	**80/20**	**70/30**	**60/40**	**50/50**	**40/60**	**0/100**
Scorch time, ts_2 (min)	4.00	5.00	5.40	8.50	8.80	10.10	16.30
Cure rate index (min^{-1})	25.0	20.0	17.85	11.80	10.90	10.10	6.40
Optimum cure time, t_{95} (min)	8.0	10.0	11.0	17.0	18.0	20.0	32.0

Determination of crosslink concentration

Figure 2 shows Mooney-Rivlin plots of $f/\left[\left(\lambda-\lambda^{-2}\right)\right]$ versus λ^{-1} for SMR-L/SBR at 100/0 blend ratio. All data in Figure 2 were experimentally obtained from 12 readings of stress-strain measurement at various pre-determined extensions. The graph was always linear according to the linear relationship between the y-axis and x-axis. From the result, elastic constant C_1 was determined by extrapolating the intercept of the graph and the crosslink concentration, $[X]_{phy}$ were calculated by the mathematical relation given in Eq. (2).

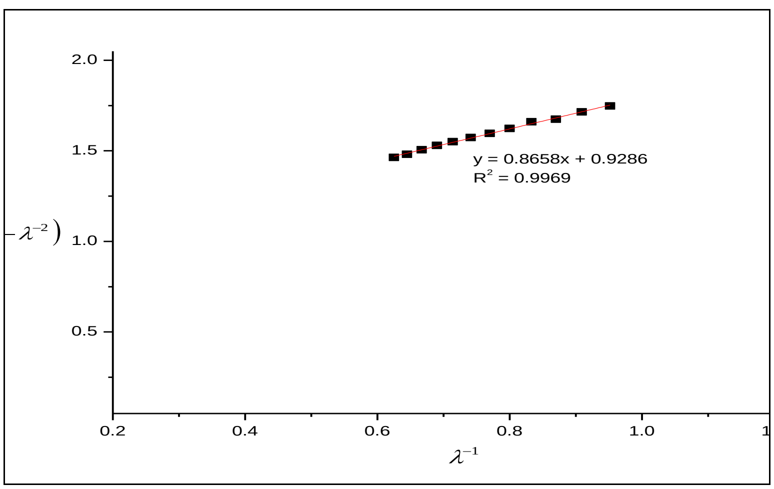

Figure 2. The relationship to determine the C_1 value from intercept of the graph

Figure 3 shows a plot of elastic constant C_1 against crosslink concentration [X]. There was a linear relationship between C_1 and [X] where C_1 increase with crosslink concentration. This linear relationship was in accord with Eq. (2) where C_1 was proportional to [X].

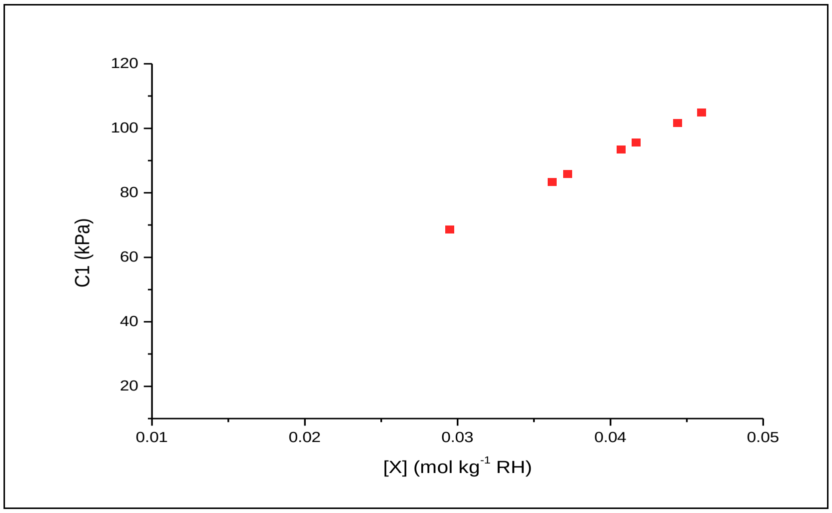

Figure 3. Relationships between elastic constant, C_1 and crosslink concentration, [X]

As the result, C_1 and [X] values were calculated as 104.8 kPa and 0.0460 mol kg^{-1} RH respectively. The calculations to determine C_1 and [X] based on this method were repeated for the other blend ratios. In Figure 4 it shows the relationship between 7 different blend ratios and the values of crosslink concentration [X]. Crosslink concentrations, [X] decreases as SBR content increases in the blend. These attributed to the fact that the degree of un-saturation of SMR-L was greater than that of SBR, which having segments of styrene [1].

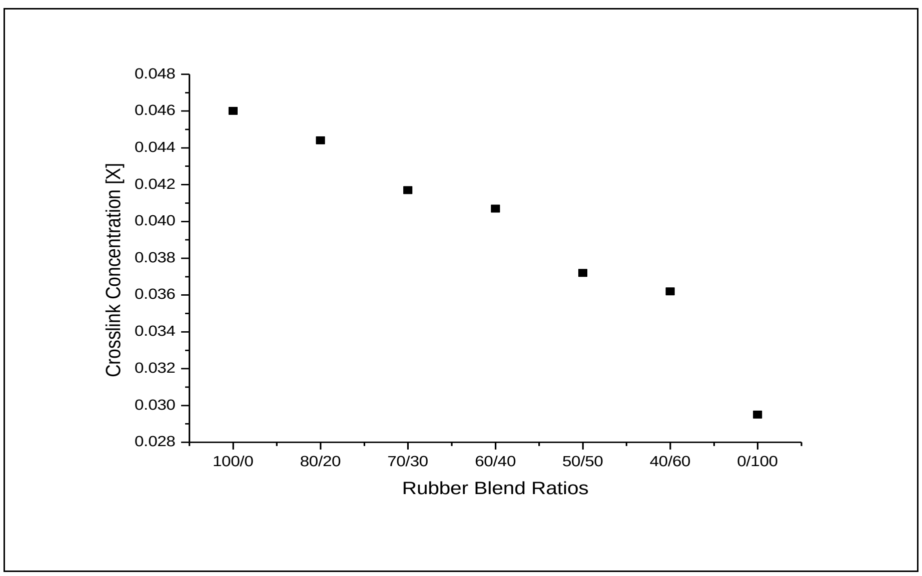

Figure 4. Relationship between crosslink concentration, [X] and rubber blend ratios by means of Equilibrium Stress-Strain measurement

Mechanical properties

Table 4 tabulated the crosslink concentration, tensile strength, hardness and resilience of SMR-L/SBR blends respectively. It can be seen clearly that the addition of SBR into the blend decreases the crosslink concentration. This resulted in the decrease of tensile properties of SMR-L/SBR blends perhaps due to the low number of chain segments at a very low crosslink concentration and hence unable to support high tensile force. As the crosslink concentration increases, more chain segments were introduced which enable to support higher tensile force [4]. Thus, tensile strength increases progressively with increasing crosslink concentration.

Evidently, the blends with high NR content exhibited better tensile properties, since NR is crystalline when stretch while SBR is amorphous. It has a good agreement with the study on tensile properties for NR/SBR blends done by Yahya et al. [6].

Table 4. SMR-L/SBR blend composition with the physical characteristics

SMR-L/SBR Blend Ratio	Crosslink Concentration, [X] (mol kg^{-1} RH)	Tensile Strength (MPa)	Hardness (IRHD)	Resilience (%)
100/0	0.0460	27.27	41.5	84.03
80/20	0.0444	18.35	41.0	83.61
70/30	0.0417	15.86	40.5	81.25
60/40	0.0407	12.82	40.0	77.79
50/50	0.0372	9.46	39.5	75.32
40/60	0.0362	7.20	39.0	73.29
0/100	0.0295	2.56	38.0	61.49

The dependence of hardness on rubber blend ratios clearly explained in Table 4. Hardness decreased as SMR-L content decreased in the blend. SMR-L with higher crosslink concentrations have higher hardness value compared to SBR with lower crosslink concentrations. High crosslink concentrations of SMR-L vulcanizate hence may attribute to a more rigid rubber vulcanizate thus increased the hardness of the rubber. These observation have a good agreement with the study done by Joseph et al. [7] which concluded that hardness have a direct proportionality with crosslink concentration.

Resilience is the ratio of energy released by the recovery from deformation to that required to produce the deformation [6]. Referring to Table 4, rebound resilience decreases as the crosslink concentration decreases. The resilience of SMR-L/SBR blend decreased upon addition of SBR into the blend. From previous study was done by Yahya et al. [6] show at low crosslink concentration the mobility of the rubber chain decreased thus increased the stiffness of the rubber vulcanizates. Therefore, lower crosslink concentration would give lower resilience.

Compatibility studies

Figure 5 shows the T_g values for the cured SMR-L/SBR blends obtained from the DSC scans. It is interesting to notice that in some of the blend samples two glass transition temperatures were detected (T_{g1} and T_{g2}). It is in a good agreement with the results reported by Goyanes et al. [8] who studied similar cured rubber blends. Based on the study, the presence of two T_g was referred to the partial immiscible blends and each one of the T_g values was associated with the corresponding phases of the blend (SMR-L phase and SBR phase). It is important to know that, most of the polymer are not miscible but are compatible as the polymer pairs achieve the desired properties.

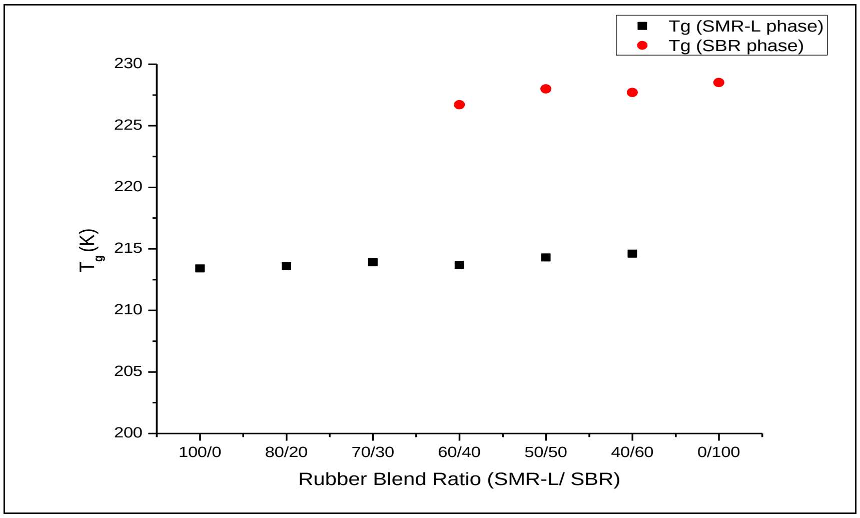

Figure 5. Glass transition temperatures, T_g as function of the SMR-L/ SBR blend ratios

Conclusion

Crosslink concentrations, [X] decreases as SBR content increases in the blend. This was based on the fact that, the degree of un-saturation of SMR-L was greater than that of SBR, which having segments of styrene. Thus, high SMR-L content in SMR-L/SBR blend gives high crosslink concentration. The study on the influence of crosslink concentration on tensile strength, hardness and rebound resilience of SMR-L/SBR blend vulcanizates showed that the mechanical properties increased linearly with the crosslink concentration. High SMR-L content in SMR-L/SBR blends resulted in higher crosslink concentration which improved the performance of mechanical properties for NR/SBR blend.

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