Compatibilization of Vulcanized SBR/NBR Blends using Cis-Polybutadiene Rubber: Influence of Blend Ratio on Elastomer Properties

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Abstract—Blends composed of styrene butadiene rubber (SBR) and acrylonitrile-butadiene rubber (NBR) were fabricated by melt blending technique using two-roll mill blend machine. Cis- polybutadiene rubber (CBR) was used as a compatibilizer for enhancing the homogeneity between SBR and NBR phases in blends. Although, no previous reports were found to discuss improving electrical properties of vulcanized SBR/NBR blends using unfilled rubber system (i.e. no fillers incorporated). Raman spectra and SEM images indicate that a significant compatibility within the rubber matrix is observed, due to using CBR compatibilizer. The effect of SBR/NBR blend ratio on curing characteristics, physico-mechanical properties, and physicochemical properties (e.g. network characteristics and thermodynamic parameters) were studied. SBR/NBR blend showed comparatively better mechanical properties, compared to each other individually in rubber system. Curing parameters e.g. Mooney viscosity and hardness were increased, while a reduction in cure time and specific gravity was observed with increasing SBR ratio in blends. Results revealed that increasing SBR resulted in an enhancement of the tensile strength, modulus at 300 % and elongation at break up to 40 phr, and then gradually decreased. The TGA results indicated that SBR/NBR blends were thermally decomposed at a temperature range of 340-520°C. The notable decrease of DC conductivity (σ_{dc}) of vulcanized blends is owing to the decrease of NBR, which is a polar portion and is responsible for increasing the conductivity of vulcanized blends. This proved that the targeted industrial applications for vulcanized blends are entirely depending upon SBR/NBR blend in elastomers matrix.

Index Terms—SBR/NBR Blends; Physicochemical Properties; Morphology; Curing Parameters; DC-Conductivity.

I. INTRODUCTION

Rubber is an important class of high polymers mostly organic; composed of long chain molecules consisting of repeating units on a backbone of carbon atoms [1]. A series of materials could be synthesized with properties entirely different from those of the blend constituents [1],[2]. Since the properties of polymer blends are fully depending on the final morphology and the interior structure of polymer matrix, thus polymer blending processes have engrossed much concern as a simple and cost-effective method for promoting novel polymer blends that have versatility and commercial purposes. Meanwhile, properties of blends can be manipulated based on their final-application by correct selection of polymer compositions [2]. Thus, one obvious advantage is that it requires a lower cost compared to the production of new polymers. The industry demands are very high that plastic producers need for providing better and huge amounts of economic materials with superior combinations of properties instead of traditional components [3]. Many research groups have recently conducted intensive studies on specific physical properties *e.g.* miscibility and phase behavior of SBR/NBR polymer blends [2]-[4]. Part of these polymers is immiscible; thus, compatibilizers are included to overcome the weak interfacial adhesion resulting in inferior mechanical properties. Furthermore, the physical properties of incorporated polymer are found in a miscible/homogenous or a heterogeneous system, which predicating on the application type. SBR and NBR blends have been employed for a long time for addressing these requirements [1]-[3].

Interestingly, it is the first time in this study compared with literatures to use the CBR as a compatibilizer rubber for (SBR/NBR) blend interaction rubber-rubber system. Some of rubber blends are immiscible due to polarity of rubber, occurring phase separation and poor interfacial adhesion between polar and non-polar rubber portions. The interfacial miscibility has been improved by incorporating of coupling agent to immiscible blend for chemical interacting with the two phases [5]. Butadiene rubber (BR) acts as a compatibilizer for heterogeneous blends and processing the separation phenomena of components. The incorporation of BR into the rubber blends has improved the cure characteristic and mechanical properties [4]-[7]. SBR is synthetic elastomeric copolymer consisting of two monomers of styrene and butadiene [5],[8]-[10]. It is a non-polar rubber that has acceptable mechanical strength, adequate abrasion resistance and good aging stability when modified with additives compared to other synthetic rubbers. SBR is one of popular materials that used in automobile tires and other specific industrial applications. It

is composed of sulfur as a curing agent [11], antioxidant [10],[11], fillers, activators and accelerators [12]. SBR/polymer blends have significance owing to their popular and useful properties for developing of new low-cost elastomeric products. Most blends are immiscible due to the lack of required interactions between the components and SBR at the interfaces, whereas a compatibilizer should been incorporated between rubber and polymer blend. Similarly, NBR is synthetic elastomers known as a polar rubber that has adequate mechanical and electrical properties [13]-[16]. It has a good anti-solvent property, compared to SBR [16]. Also, it is one of the most important rubber types which have commercial importance because of its utility in a lot of industrial applications like hoses, cables industry and other applications [14],[16]. Recently, researchers have pioneered the impact of SBR/NBR blends on the physicochemical properties of blends. Mansour *et al.* [1], have investigated the effect of unsaturated polyester as compatibilizer on SBR/NBR blends, while Ramesan *et al.* [2], reported the influence of SBR/NBR blends with/without compatibilizer used. Electrical properties *e.g.* electrical conductivity of acrylonitrile butadiene rubber loaded carbon black has been studied by Morsy and Ismail [17]. They revealed that the electrical conductivity of NBR without compatibilizer was significantly enhanced due to presence of the butadiene rubber (CBR) which acts as a compatibilizer [18].

In the current study, we are investigating the improvement of physical and physicochemical properties of vulcanized SBR/NBR blends compatibilized with CBR, owing to alteration of blend ratio of elastomers. Furthermore, DC-electrical conductivity has been discussed to determine the initial electrical properties of the prepared vulcanized SBR/NBR blends, while intensive electrical properties will be discussed in details in an extended work.

II. EXPERIMENTAL PROCEDURES

A. Materials

SBR (SBR-1502, Sp.Gr. 0.945, styrene content 23.5%, ML (1+4) of 48-58 at 100 ºC) (M_n 125.6 kDa, M_w 359.5 kDa, and M_z 996 kDa) and NBR (NBR-Perbunan™, Bayer AG., Germany) (acrylonitrile content 34%, density 0.99 g/cm^3, ML (1+4) of 65 at 100 ºC) (M_n 103.1 kDa, M_w 268.9 kDa, and M_z 801.4 kDa) were donated from Transportation and Engineering Co., (TRENCO, Alexandria, Egypt). *Cis*-1,4-polybutadiene rubber (CBR) was supplied by Bayer AG Germany. Both sulfur, stearic acid and zinc oxide were used in commercial grade without purification and locally manufactured by ADWIC Co. Egypt.

The preparation of six different formulations of SBR/NBR blends was carried out according to standard test method for rubber evaluation of SBR (ASTM D 3185–99) using mixing cycle as shown in (S1, supplementary

materials). The addition of 10 *phr* paraffinic oil into the rubber compound serves as plasticizer or softener in order to decreases the shore hardness of the final blend (Table I). All rubber components have been supplied, weighed and mixed on a laboratory-mill at TRENCO Company (Alexandria, Egypt) with dimensions: outside diameter 460 mm, work distance 250 mm, slow roll speed of 16 rpm and gear ratio 1.4.

The mill has been adjusted by rolling temperature control. The compositions of blends for vulcanization step are listed in Table I. Additionally, Fig. 1 shows a simple schematic diagram for exhibiting the vulcanization of SBR/NBR blends. Before each test, all SBR/NBR blends were vulcanized using a hot-press at 153 ± 2ºC for 30 minutes by means of standard test method in accordance with (ASTM D-3191).
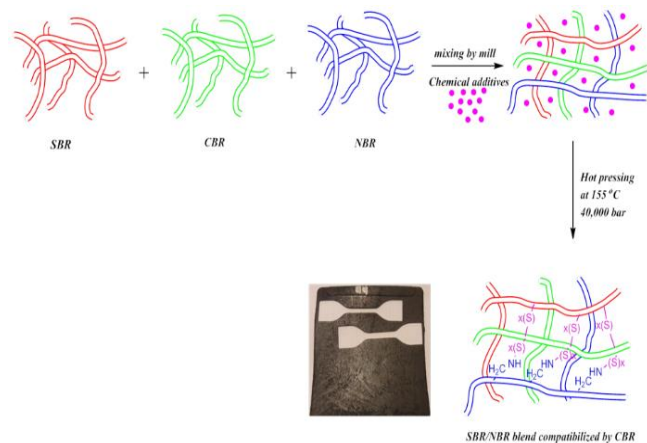

Fig. 1. Schematic diagram for vulcanization of SBR/NBR blend compatibilized by CBR.

B. Rheometric Measurements

Vulcanization parameters were measured by using (MDR-2000; version 1.00, England) with temperature range 100-200 °C according to standard method (*ASTM* D-5289).

C. Raman Spectroscopy

Raman spectroscopy analysis was done at room temperature (Senterra-Raman spectrometer, Bruker, Germany) with a 514.5 nm excitation wavelength and power output of 10 mW at room temperature to determine the shifting peak of the prepared material. Each measurement was taken in the range of wavenumbers from 4000- 400 cm^{-1}.

D. Scanning Electron Microscope (SEM)

The surface morphology of SBR/NBR blends was investigated by SEM (type: JEOL, JSM-6360LA, Japan with 15 kV). The SBR/NBR blends were coated with by Au using an ion sputter coater (model: 11430, USA, combined with vacuum base unit or SPi module control, model: 11425, USA).

TABLE I: SBR/NBR BLENDS VULCANIZATION RECIPE

Sample Name	Blends composition SBR/NBR	Chemicals Additives (phr)*						
		CBR	ZnO	Stearic acid	paraffinic oil	6PPD[a]	MBTS[b]	S[c]
0/100	0/100	10	5	2	10	1	2	2
20/80	20/80	10	5	2	10	1	2	2
40/60	40/60	10	5	2	10	1	2	2

60/40	60/40	10	5	2	10	1	2	2
80/20	80/20	10	5	2	10	1	2	2
100/0	100/0	10	5	2	10	1	2	2

a) N-(1,3-Dimethylbutyl)-N'-phenyl-p-henylenediamine, b) Mercapto-benzothiazol disulfide, and c) Sulfur. *phr: means that each ingredient in grams must be added to 100 g of total rubber composition.

E. Thermogravimetric Analysis (TGA)

TGA samples were carried out by (Shimadzu TGA-50, Japan) analyzer at a heating rate of 10ºC/min under nitrogen, and the temperature range was from room temperature up to 750 ºC. The samples were heated from 25-750 ºC with 10ºC/min. The purge nitrogen gas rate was operated at 10 mL/min to 550 ºC and oxygen 10 mL/min to 750 ºC. The decomposition temperature (T_d), the weight loss %, and the thermal onset temperature (T_{onset}) of decompositions were determined to describe the thermal stability of rubber blends. T_{onset} is defined as the temperature at the intersection of the baseline mass and tangent drawn to the mass curve at the inflection point or point of the greatest rate of mass loss % [19].

F. Mechanical Properties

The mechanical properties of vulcanized blends were described by measuring tensile strength, modulus at 300%, elongation at break and hardness, while specific gravity was measured as physic-mechanical properties for blends. The Mooney viscosity was measured using (MV-2000, England) with rotor speed 2 *rpm* and calibrated temperature 100-200ºC. The tensile of blends were measured on a Monsanto Tenso-meter (capacity 10 KN and deformation rate of 60 mm min^{-1}) according to (ASTM D-412) at room temperature. Samples were prepared by cutting three individual dumbbell shape specimens from the vulcanized sheets. The minimum thickness ($\sim 3mm$) was determined using a dial-gauge. The hardness measurements were performed by a Durometer in Shore according to (ASTM D-2240). A system was performed by hand-time at which the reading was taken for 15 sec. All measurements were taken triplicate and the average values were reported. *Sp.Gr.* were determined using (E. Mettler, Zurich, Switzerland) and the used empirical specific gravimetric equation is given as follows:

$$Sp.Gr. = \left[\frac{W_a}{W_a - W_w}\right]\rho_w, \tag{1}$$

where, W_a is weight of the sample in air, W_w is weight of the sample in water and ρ_w is water density.

G. Physicochemical Properties

Swelling measurement

Strips dimensions (0.2×0.5×2 cm^3) were immersed in benzene and water at room temperature for one day. The maximum degree of swelling is measured using the following relation of the maximum volumetric swelling equation [20].

$$Q_m\% = \frac{M_s - M_d}{M_d} \times 100, \tag{2}$$

where, M_s and M_d are mass of swell and dry pieces of rubber, respectively.

H. Crosslink Density Calculation

Cured test pieces of dimensions ($0.2 \times 0.5 \times 2$ cm^3) were weighed and each sample was immersed in 30 mL benzene at room temperature. The swollen-sample was kept in the dark for avoiding oxidation. The sample was detached from benzene and the excess benzene was removed by soft paper. The samples were then kept in a closed vessel to prevent benzene's evaporation and the weights of the swollen samples were determined at intervals time. The swelling data have been taken to calculate the molecular weight between two adjacent crosslinkers (M_c) using the *Flory–Rehner* equation [18]

$$M_c = \frac{-\rho_p V_s V_r^{1/3}}{\ln(1 - V_r) + V_r + \chi V_r^2}, \tag{3}$$

where, ρ_p is the rubber density, V_s is the molar volume of benzene, χ is the interaction parameter of rubber, and V_r is the volume fraction of the swollen rubber which is given as follows, where, Q_m is the weight change of the SBR/NBR blends in benzene.

$$V_r = \frac{1}{1 + Q_m}. \tag{4}$$

The crosslinking density (V) is given by the following equation [18].

$$V = 1/(2M_c) \text{ mol cm}^{-3} \tag{5}$$

The next parameters were used to determine the crosslinking density of SBR/NBR. ρ(SBR)= 0.945 gm/cm^3, ρ(NBR) = 1gm/cm^3, χ (SBR)= 0.343, χ (NBR)= 0.390, V_s (benzene) = 89.115 cm^3/mole.

I. Thermodynamics calculations

The change in elastic Gibbs free energy was calculated using Flory-Huggins equation [20].

$$\Delta G = RT\left[\ln(1 - V_r) + V_r + \chi V_r^2\right], \tag{6}$$

where R is a general gas constant and T is the temperature in Kelvin.

From the statistical theory of rubber elasticity, the conformational entropy ΔS was calculated by the following entropy equation [20].

$$\Delta S = -\frac{\Delta G}{T} \tag{7}$$

J. Electrical Characteristics

The electrical measurements were carried out using DC voltage/current generator along with a precision digital electrometer (model: 616, Keithley Instruments Inc., Cleveland, Ohio, USA). The disk sample dimension for electrical conductivity measurements are as (1.6 cm diam.,

0.3 cm thick). Samples are coated with silver-paste and are showed an ohmic contact with rubber [21]. The sample holder consists of brass holder and electrode. The direct current conductivity σ_{dc} is calculated using the DC conductivity relation as follows:

$$\sigma_{dc} = \frac{d}{RA}, \tag{8}$$

where d is the sample thickness in meter, A is the sample surface area in m^2 and R is the resistance in ohm.

TABLE II: VULCANIZATION CHARACTERISTICS OF SBR/NBR BLENDS

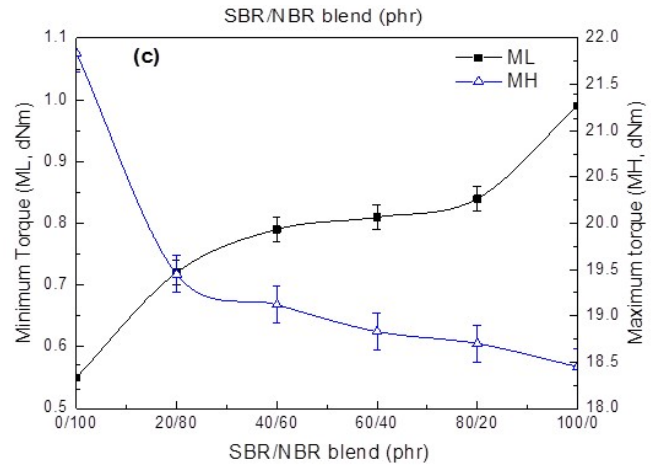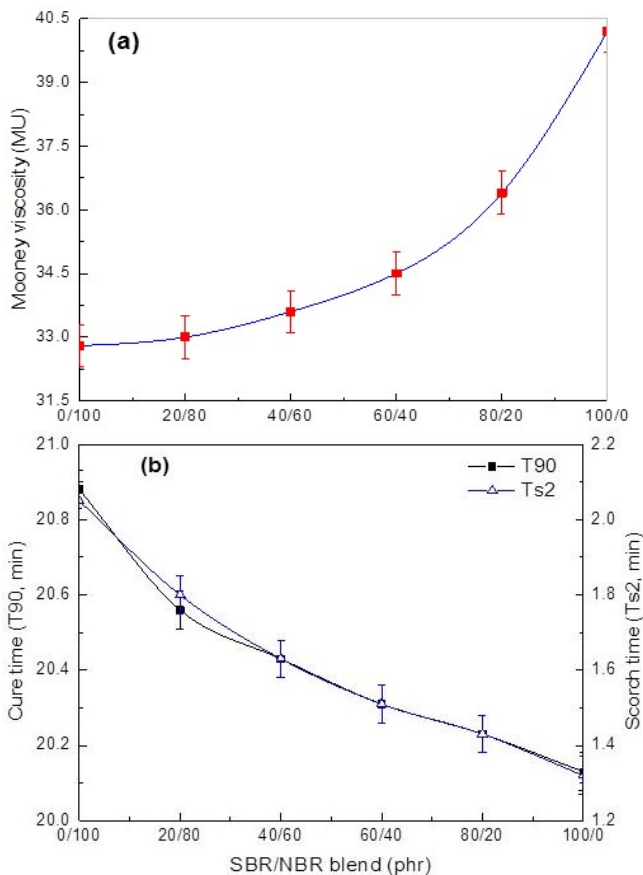| Blend ratio SBR/NBR	MV (MU)	ML (dNm)	MH (dNm)	TS2 (min)	T90 (min)
0/100	32.8	0.55	21.84	2.05	20.88
20/80	33.0	0.76	19.45	1.91	20.56
40/60	33.6	0.79	19.17	1.63	20.43
60/40	34.4	0.82	19.02	1.51	20.31
80/20	36.4	0.84	18.83	1.43	20.23
100/0	40.2	0.85	18.70	1.32	20.13

Fig. 2. Effect of the SBR/NBR blend ratio on curing parameters a) Mooney viscosity (MV), b) curing time (T90) and scorch time (TS2), and c) minimum torque (ML) and maximum torque (MH).

III. RESULTS AND DISCUSSION

A. Curing Characteristics of SBR/NBR Blends

Curing parameters *e.g.* Mooney viscosity (MV), curing time (T90), scorch time (TS2), minimum torque (ML), and maximum torque (MH) change notably with blend compositions were given in Table II and shown by the rheographs of the mixes in Fig. 2. In all blend compositions, a relatively high optimum torque is obtained when concentration of NBR in the blend is increased. It is reported that, the maximum torque is dependent on crosslinking density and nitrile group which is crosslinked with SBR, so the degree of crosslinking increased by increasing NBR content [22]. As a result of high molecular weight of SBR, the long chain tends to coil. These results are consistent with obtained results of Zulkepli and Ismail [22]. They have revealed that MH was slightly increased with NBR content in SBR/NBR blends owing to the contribution of nitrile group in the crosslinking process of blend. The different portions of SBR chains entangle with the chain of NBR and its own chains. Thus, low NBR content causes less extent of engagement of SBR/NBR blends which results in an increase in MV, ML values and a decrease in MH, TS2 and T90 values (Figs. 2a-c), and then this behavior is used for accelerating the vulcanization process. These results are consistent with that obtained by Ismail *et al.* [23]. They have reported that TS2 and T90 values of SBR/NBR blends increased with increasing of NBR ratio in blends owing to the polarity of NBR. As ratio is increased, the curative agent (*i.e.* sulphur) becomes less soluble in NBR compared with SBR rubber nature.

B. Raman Spectroscopy of Vulcanized SBR/NBR Blends

Raman spectra of SBR/NBR rubber blends are illustrated in Fig. 3. Basically, SBR and NBR are reported to encounter fluorescence and transparency problems in rubber blend systems, thus they could not be measured by FTIR [2],[3],[7]. Fig. 3 shows the Raman spectra of vulcanized SBR/NBR blend system, showing a relatively good quality spectrum, where both styrene groups of SBR and acrylonitrile groups are clearly visible in these spectra. The main feature in the NBR is the presence of acrylonitrile spectrum v (C ≡ N) stretch at 2240 cm^{-1}. Also, the butadiene

species of compatibilizer is predominantly *trans* in the NBR rubber [24],[25]. It showed the characteristic C-S stretches at 600 cm^{-1}, disulfide bond stretches at 500 cm^{-1} and N-S bond stretches at 700 cm^{-1}. The band at 968 cm^{-1} stands for the *trans* CH=CH and the C = C stretching frequency appears at 1653 cm^{-1}. It is suggested that the polar-polar interactions between the chlorine of CBR and cyanide group of acrylonitrile repeating units which present in NBR in order to lead to the miscibility in blends. As seen, pure NBR and SBR/NBR blends show absorption at 2337 cm^{-1} due to CN stretching and N-H appears at 2500 cm^{-1}.
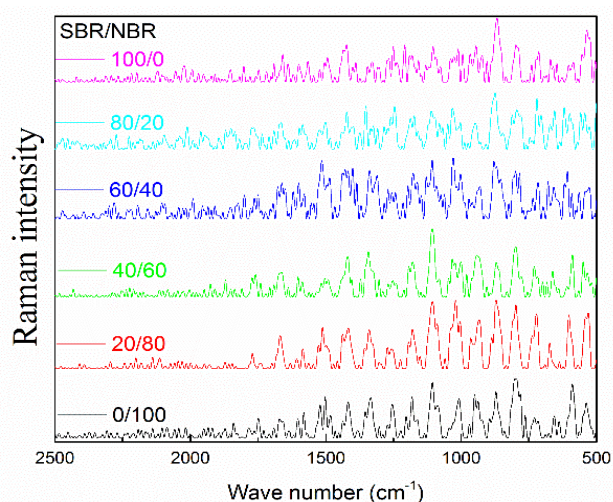

Fig. 3. Raman spectra of vulcanized SBR/NBR rubber blend ratios as 0/100, 20/80, 40/60, 60/40, 80/20 and 100/0, respectively.

C. Morphology Investigation of Vulcanized SBR/NBR Blends by SEM

SEM was performed as a helpful tool for better understanding the extent of the CBR influences compatibilization degree of immiscible blends. Fig. 4 presents SEM micrographs for the investigated SBR/NBR blends surface. As expected, the introduction of the CBR compatibilizer might cause a humble enhancement in the miscibility between the blend phases (Figs. 4a-c). Accordingly, CBR content decreases the domain size to a high extent and increases the permeation properties between phases in blends, and then the system exhibits similar and more homogenous surface morphology in case of presence of two phases of blends (*i.e.* SBR and NBR, simultaneously). Figs. 4b and 4c show that the blends seem to be more compatible with each other and can reflect the emersion of reasonable interfacial interactions at the contact boundaries between the phases. It might be attributed to presence of the CBR at the interface to participate in lowering the interfacial tension between the phases. As a result, the absence of one of the phases as spherical domains dispersed in the other phase. This might indicate a possible change from the dispersed morphology (Figs. 4a, 4d) to coherent and uniform surface morphology (Figs. 4b, 4c). The morphology results are entirely in good agreement with that obtained by Essawy *et al.* [26], who have investigated the effect of introduction of MMT clay contents on morphology improvement of SBR/NBR blends.
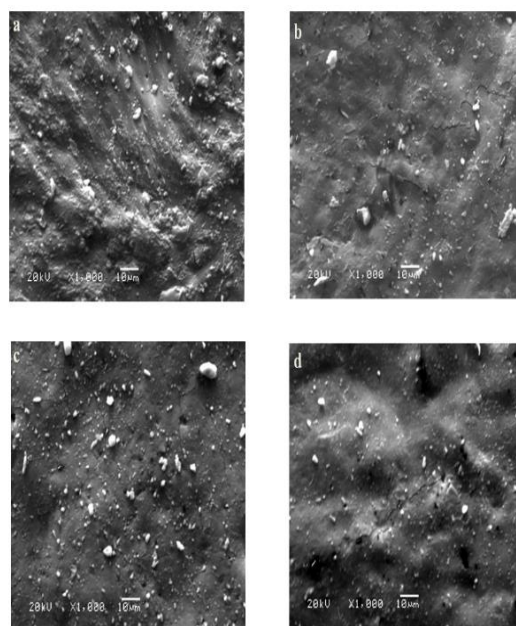

Fig. 4. SEM micrographs of vulcanized SBR/NBR blends with different SBR: NBR ratios as follows: a) 0/100, b) 20/80, c) 40/60 and d) 100/0 (Original magnification 1000×).

D. TGA Results of Vulcanized SBR/NBR Blends

The thermal stability of SBR/NBR blends was performed by TGA analysis as function of blend ratio and is shown in Fig. 5, while the thermograms results were summarized in Table III. It was noticed that, all blends show a similar decomposition process. Generally, SBR/NBR blends have improved the first decomposition stage in comparison to SBR alone. This thermal behaviour reveals that the rubber blends are highly reluctance to moisture absorption due to incorporation of bulky structure onto the rubber chains. Notably, the vulcanized blend compounds were thermally decomposed ranged between ~ 340-520 ℃ and then over 550 ℃. Where, all polymers are pyrolyzed into 0 %, excluding the effect of inorganic fillers and carbon black which remain inside the samples. Precisely, thermal degradation of SBR/NBR occurred in two main degradation stages. The real first stage started at 340 ℃ with a weight loss of 8 % and completed at ~ 500 ℃ with a weight loss > 75%. In the second degradation stage, the degradation took place at > 520 and completed at 650 ℃ with the rest of sample weigh was completely burned and converted to ash. The two decomposition stages consistent with degradation by random-chain scission of the butadiene and the nature of AN parts in NBR. In addition, there are such strong electronegative groups (nitrile groups in NBR) that resulted in relatively high interaction and high heat resistance in elastomers. Therefore, NBR has endured high thermal stability compared to SBR owing to the fact that NBR possesses higher butadiene content than SBR. Inspecting of Table III, reveals that both T_d of the 50% weight loss and T_{onset} decomposition temperatures are gradually enhanced with increasing NBR portion in blends ranged between ~460-470 ℃ and 340-420℃, respectively. However, they are significantly reduced with incorporation of SBR in blends.

These results are consistent with that reported by Lee *et al.* [27], who have revealed insufficient thermal stability for

NR/SBR/BR blends with incorporating SBR. Also, the beginning temperature of the 2nd decomposition stage decreased dramatically (varied from 417 ºC to 340 ºC), with reduction of the NBR portion in vulcanized blends. This speculation could be explained by the fact that the NBR is usually used as a heat-resistance composition in manufacturing of automobile tires, compared to SBR rubber. This conclusion is slightly agreed with reports of Alneamah and Almaamori [28]. They have reported that, NBR is initially thermal degraded at 360 ºC in the first degradation stage, while it has been improved into 368 ºC with incorporating polyimide. Furthermore, no notable change in weight loss % has been noticed due to blends altering in the 2nd decomposition stage. No alteration in the 3rd decomposition stage has been detected, where the remained polymer mass showed a complete thermally degradation due to carbonization and volatilization processes which ranged between 525-750 ºC for all vulcanized blends.

TABLE III: TGA RESULTS OF VULCANIZED SBR/NBR BLENDS

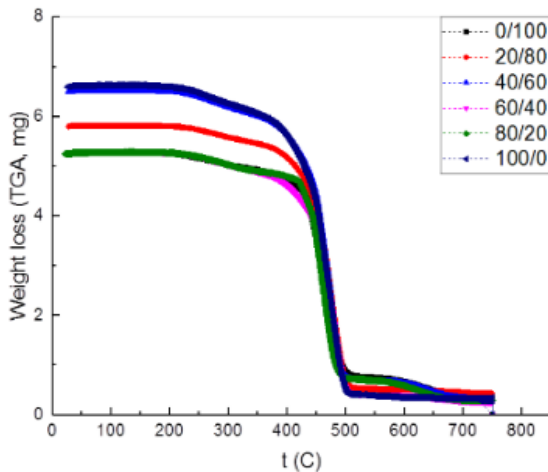| Blends ratio SBR/NBR	T_dºC, (weight lose %)		T_d, ºC (weight loss 50%),	T_{onset}, ºC
	1st decomposition stage	2nd decomposition stage		
0/100	28-383, (8 %)	417-508, (75 %)	470	420
20/80	28-389, (6 %)	387-500, (85%)	469	416
40/60	28-375, (9 %)	375-518, (84 %)	465	375
60/40	28-352 (7.5 %)	352-508, (84 %)	464	352
80/20	28-354, (10 %)	355-505, (75 %)	461	355
100/0	28-343, (8 %)	343-506, (86 %)	460	340

Fig. 5. TGA thermographs of SBR/NBR blend ratios.

E. Mechanical Properties of Vulcanized SBR/NBR Blends

The effect of blend ratio on the physico-mechanical properties of vulcanized SBR/NBR blends is presented in Fig. 6. It is clear that increase of SBR ratio exhibits a makeable increasing of TS, M_{300} and Eb for blend ratios of 0/100, 20/80 and 40/60 Figs. 6a, 6b. This is attributed to the increase of the crosslinking density of SBR/NBR matrix is corresponding to increasing SBR content. For blends 60/40, 80/20 and 100/0, the increase of SBR reduced significantly TS, M_{300} and Eb owing to the lowering of polarity effect of NBR upon increasing SBR content Fig. 6a [8]. Fig. 6b shows the dependence of hardness on the blend ratio of SBR and NBR. It is observed that increasing the SBR ratio in blends exhibits hardness increment, which is agree with that obtained by Findic *et al* [29]. They have assumed that SBR possesses butadiene copolymer rubber and styrene group which act as a harder block to increase the hardness of SBR blend matrix [29]. Comparing the specific gravities of NBR (~1.21) and SBR (~1.033); the decrease of the specific gravity with increasing SBR content (Fig. 6c), verifies pretty well the mixing law.
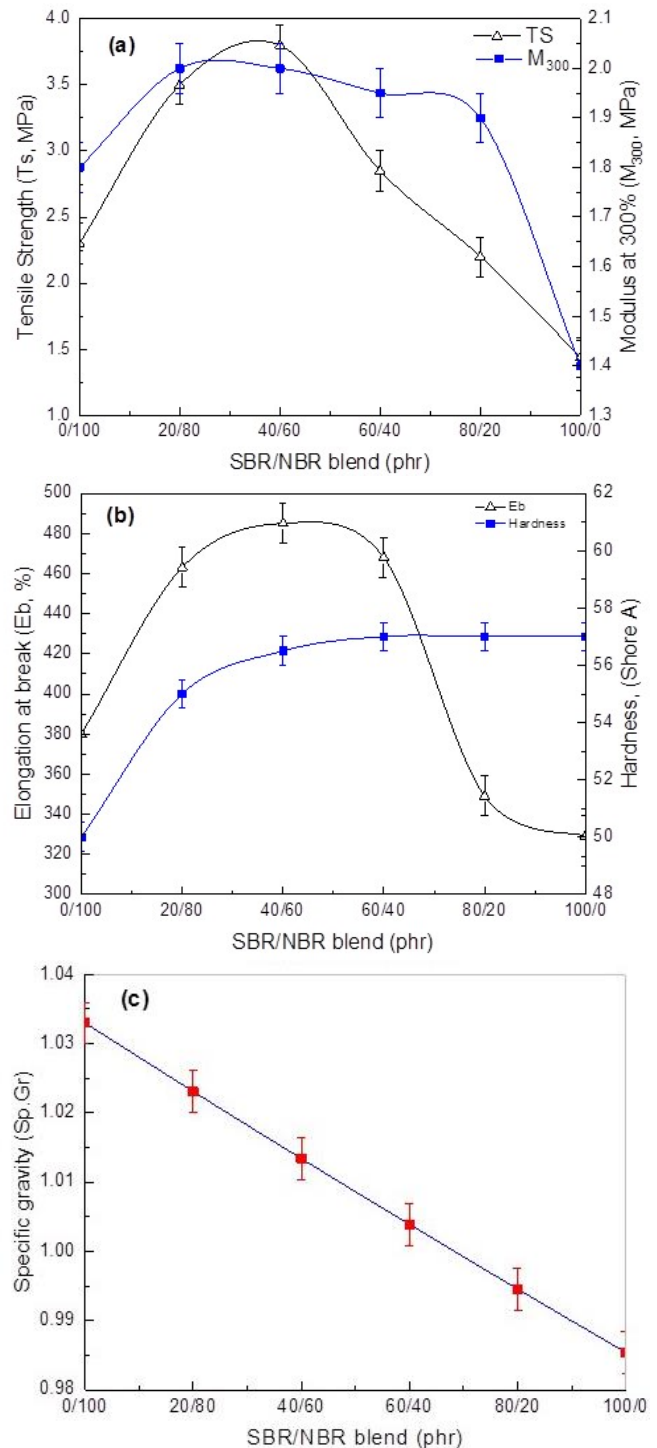

Fig.6. Effect of the SBR/NBR blend ratios on a) tensile strength (TS) and modulus at 300% (M_{300}), b) elongation at break (Eb) and hardness, and c) specific gravity (*Sp. Gr.*) of vulcanized SBR/NBR blends.
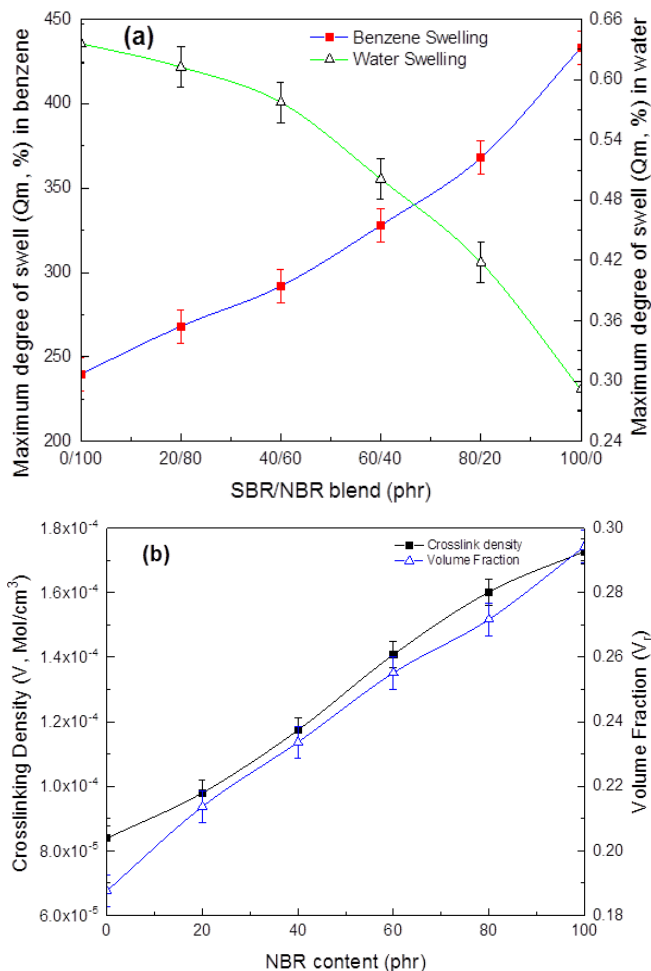
Fig. 7. Effect of SBR/NBR blend ratios on a) maximum degree of swell (Q_m %) in benzene and water and b) crosslinking density and volume fraction V_r of vulcanized SBR/NBR blends.

It is expected that the blends possess intermediate *Sp.Gr.* values between those of SBR and NBR values, thus the increase of SBR ratio in the blend tends to reach the extreme value of specific gravity of SBR. In overall, the improvement in the mechanical properties could be attributed to the enhancement in interfacial adhesion of SBR/NBR blends which is given by reduction of the interfacial energy between phases as a result of introduction of CBR [3].

TABLE IV: NETWORK CHARACTERISTICS AND PHYSICO-CHEMICAL PARAMETERS OF VULCANIZED SBR/NBR BLENDS

SBR/NBR blend ratio	V_r	M_C	Crosslinking Density × 10⁻⁴	ΔG (J/mol)	ΔS (J/mol/K)
0/100	0.29	2893.70	1.73	-55.80	0.19
20/80	0.27	3121.53	1.60	-45.31	0.15
40/60	0.26	3551.84	1.41	-38.56	0.13
60/40	0.23	4259.31	1.17	-30.88	0.10
80/20	0.21	5103.74	0.98	-24.73	0.08
100/0	0.19	5958.41	0.84	-18.0	0.06

F. Network characteristics and physico-chemical parameters of vulcanized SBR/NBR blends.

The formation of physical and chemical crosslinking between macromolecules through SBR/NBR blends is measured from crosslinking density which is calculated by Flory–Rehner equation (Eq. 3). The swelling capacity or degree could be herein explained depending upon the theory of polarity. It was also of importance to show the effect of solvent type and its polarity on the swelling of SBR/NBR blends. Fig. 7a shows the variation of maximum degree of swelling in benzene and water (Q_m (%) upon SBR/NBR different ratios. The obvious increase of Q_m % in benzene might be attributed to the fact that SBR rubber is non-polar [23], so high SBR blends absorb more non-polar solvent. Basically, due to the hydrophobic characteristic of rubber therefore the swelling of SBR/NBR blends in water could be neglected, where swelling ratio is ranged in a very small scale (Q_m % ~ 0.3-0.7%). However, Q_m (%) in water increases slightly with increasing of NBR content, because NBR rubber is polar, so it is able to absorb more polar solvent (Fig. 7a). The crosslinking density decreases with decreasing the volume fraction of amorphous swollen phase of SBR ratio in blends. Subsequently, it is evident that the crosslink density of blends increases progressively with increasing NBR ratio in vulcanized blends (Fig. 7b). This assumption is attributed to exist of nitrile in NBR rubber which increases the degree of crosslinking. These results are consistent with that obtained by Botros *et al* [30]. They have found that crosslinking density of non-compatibilized SBR/NBR blends have enhanced by increasing of NBR ratio in blends. Also, it is owing to the contribution of nitrile groups in NBR to accelerate crosslinking process. Unlike, our results are not consistent with the results of El-Sabbagh *et al* [31], who have found that crosslinking density of NR/SBR vulcanized blends is increased with increasing the SBR ratio in blends. The physicochemical parameters of SBR/NBR blends are illustrated in Table IV. According to the listed data, it is obvious that the high negative change in free energy values (ΔG) are the most compatibility between the blends. By increasing the SBR content, the interfacial area increased up to a certain extent, due to the bulky structure of SBR. On then may point out that a thermodynamic stable system is formed when $\Delta G < 0$ [32]. It was found that the ΔG in negative values are obtained as the concentration of NBR increases in blends. Furthermore, it is revealed that CBR acts as a compatibilizer agent in the immiscible SBR/ NBR blend system. Similarly, ΔS values also increase as the concentration of NBR increases in blends. The increase in entropy gives an evident on the disorder of the system which also reveals the enhanced compatibility. However, the disorder of the system increases due to the incorporation of NBR into the SBR/NBR matrix [21].

G. DC Conductivity of Vulcanized SBR/NBR Blends

Electrical conductivity of the vulcanized SBR/NBR blend sheets with different compositions are shown in Fig. 8. Basically, electrical charge displacements in the bulk rubber materials produce two types of featured physical phenomena: (*i*) If the charge motion is harshly restricted to a localized volume of the matter, followed by polarization occurred; or (*ii*) if charges are collectively diffuse through long distances, then diffusion is possible and DC conductivity σ_{dc}, is recognized. Thus, the explanation of DC conductivity of blend sheets is mainly based on the polarization of tested sheet composition. Furthermore, presence of the electro-negative nitrile groups in NBR which corresponded to interaction and conductivity occurred [28],[32]. As seen, it is clearly detected that the electrical

conductivity of the SBR/NBR blends increase with increasing NBR content. Because of NBR is polar and has electrical conductivity in the order of 10^{-10} Ω^{-1} cm^{-1}, however, SBR is non-polar and has low electrical conductivity between (10^{-14} $\Omega^{-1}cm^{-1}$: 10^{-16} $\Omega^{-1}cm^{-1}$) [32]. Thus, increasing of NBR content shows an increase in the polarity of blends owing to the increase of $C \equiv N$ dipoles which might increase the conductivity of SBR/NBR blend matrices. The values of σ for the intermediate blends confirm the aforementioned speculation of mixing between the conductivity of NBR and that of SBR.
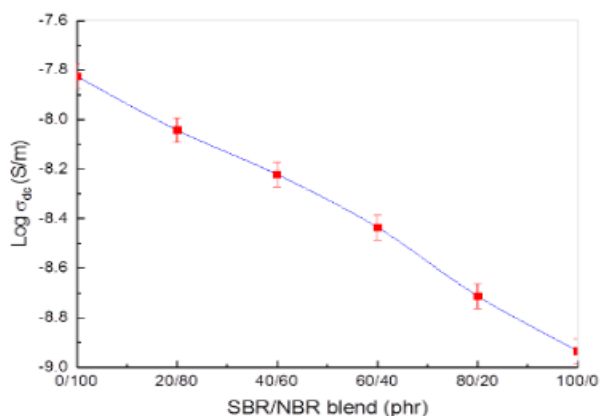

Fig. 8. DC electrical conductivity of vulcanized SBR/NBR blends.

IV. CONCLUSION

In conclusion, the incorporation of SBR in rubber blends decreases the scorch time, cure time and improves the mechanical properties, where increasing SBR content enhances TS, M300 and Eb of SBR/NBR blends in comparison with NBR and SBR rubber without blending. Raman spectra and SEM analysis indicated that it has been a good compatibility within the rubber matrix because CBR acts as a compatibilized and sulfur accelerated the crosslinking between blend compositions. Interestingly, TGA analysis showed that thermal properties of SBR/NBR have been improved by increasing NBR ratios in blends. As expected, the swelling ability of vulcanized blends in benzene increased by increasing SBR ratio owing to the fact that SBR is non-polar portion. On the contrary, Qm in water decreases with increasing SBR content of SBR/NBR blends due to the polarity of NBR. Furthermore, the significant decrease in DC conductivity (σdc) is owing to the decrease of NBR polar ratio in vulcanized blends, which is responsible for increasing the conductivity values. The remarkable enhancement in the physical properties of all investigated samples could be used in different applications such as, mechanical shock absorbers, manufacturing of automobile tires and cars spare parts.

APPENDIX

SBR/NBR blend was mixed according to standard test method for rubber evaluation of SBR (ASTM D 3185–99) using mixing cycle as follows: The mixing procedure was carried using a two-roll mill at room temperature. First stage is known as mastication process; the mill nips were set at 0.20 mm wide then raw SBR is passed through the mill nip. After mastication, the processing will be easier and the effectiveness of dispersion of compounding ingredients is significantly increased (mastication time ~2 minutes). This is important to soften the SBR before adding further ingredients then CBR compatibilizer is incorporated for 3 minutes and finally NBR for 5 min. Second stage, zinc oxides and stearic acid were added evenly into the rubber compound (compounding time, ~ 5 minutes). Next, the other chemical ingredients were added (compounding time ~ 12 minutes). Lastly, the sulfur was gradually added into blend. Then, the rubber compounds were roll at opening mill nip stepwise until thickness (2.5 mm). The total mixing process was done approximately in 31 minutes.

CONFLICTS OF INTEREST

The authors report that no financial or nonfinancial conflict of interest.

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