



Investigation of natural rubber compatibility with different types of butyl rubber

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Abstract

This study aims to evaluate the compatibility of natural rubber (NR) with different types of rubbers, including butyl rubber (IIR) as a nonpolar rubber, bromobutyl rubber (BIIR) and chlorobutyl rubber (CIIR) as polar rubbers. The NR/ IIR, NR/ BIIR, and NR/ CIIR blends were prepared with different blend ratios. The compatibility of the blends under investigation was evaluated by different physical techniques. To overcome the problem of incompatibility (phase separation) a third component was added as a compatibilizing agent to these blends, such as styrene-butadiene-styrene (SBS) block copolymer and maleic anhydride (MAH). The compatibility of such blends with and without different compatibilizers was assessed by rheometric characteristics; mismatch factor (M_f), physico-mechanical properties, scanning electron microscopy (SEM) and heat of mixing data. The results of all these techniques were discussed. The overall results demonstrate that the addition of a small percentage of SBS and MAH as compatibilizers have decreased the domain size of the dispersed phase and increased the interfacial adhesion between the blend phases. Consequently, the compatibility, morphology and physico-mechanical properties of the investigated blends are noticeably improved.

Keywords: Natural rubber; Butyl rubber; Blends; Styrene-butadiene-styrene; Maleic anhydride.

1. Introduction

An emerging research trend is the development of novel rubber products through the efficient blending of two or more rubbers. However, combining two incompatible rubbers results in a composite with inferior mechanical properties. The addition of an appropriate compatibilizer during the processing stage can greatly improve the mechanical and other crucial aspects of such blends. The copolymers used as the compatibilizers can be a block, graft, or random copolymer with a segment that is chemically equivalent to that of the phase in consideration. These compatibilizers increase the interfacial adhesion between phases which in turn decrease the dispersed domain phase matrix and reduce the macroscopic inhomogeneity. To achieve optimum compatibility between two incompatible rubbers, the choice of a suitable copolymer as a compatibilizer for rubber blend is essential. An efficient compatibilizer must meet specific criteria, including being present at the interface between phases, fine dispersion during mixing, providing stability against gross separation, and improving adhesion between the blend components. Effective compatibilizers should provide an intermediate phase between the incompatible rubbers, allowing induced

stresses to be transferred between the phases via covalent bonds between the phases [1-7].

Due to the usefulness of creating new materials with desirable features lacking in the component rubber, the importance of blending two types of rubber has lately expanded. Blend compositions and processing conditions influence polymer blend attributes, which can be managed. Natural rubber is also widely utilized and has several benefits, such as flexibility. Natural rubber (NR) and other rubber mixtures has been the subject of several investigations [8-11]. On the other hand, Tire manufacturing is one very fascinating example. Natural rubber (NR) and synthetic rubber (such as IIR, BIIR, and CIIR, etc.) can be blended to improve building characteristics like tensile strength, tear strength, resilience, fatigue fracture, etc. Fillers can be divided into white (non-black) or black (black). In the rubber business, black fillers are more frequently used than white fillers. It is employed by the cable, hose, and tyre industries. In the meanwhile, the automobile, general rubber goods, and footwear industries all employ white fillers. The goals of polymer blends include enhancing their physical and mechanical properties, swelling characteristics, cost-effectiveness, high ageing characteristics, and long service life. As a result of the lack of interactions

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Receive Date: 25 August 2022, Revise Date: 03 September 2022, Accept Date: 06 September 2022

DOI: 10.21608/EJCHEM.2022.158454.6850

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between blends' constituent parts at the interfaces, the majority of polymer blends are immiscible; therefore, compatibilizers should be introduced between the components of blends. The final physico-mechanical characteristics of polymer blends are mostly determined by the robust interactions between the blend's components. The main distinction between the three types of polymer blends—totally miscible, moderately miscible, and entirely immiscible—relates to their phase structure. Homogeneity is seen in entirely thermodynamically miscible mixtures at least on the Nano scale, if not at the molecular level [12]. On the other hand, polymer blends are being extensively studied and utilized in a variety of industrial and other applications. In many industrial applications, the durability and efficiency of products are greatly influenced by their mechanical strength, thermal stability, and barrier qualities of the polymer [13]. Similar to copolymers, these blends allow you to combine the properties of various components into one product. The compatibilizing chemicals are widely used to stabilize multiphase polymer systems, which are quite prevalent. Graft or block copolymers are frequently used as compatibilizers to change immiscible polymer mixes. It can usually serve as "interfacial agents" and enhance the interfacial interaction between the phases of the immiscible blend components. [14, 15]. Butyl rubber (IIR) is the copolymer of isobutylene and a small amount of isoprene. As a result the unsaturation between the long polyisobutylene segments is minimized. Butyl rubber has high air impermeability, retention and excellent flex capabilities. The synthesis of halogenated butyl rubber (halobutyl) greatly increased the utility of butyl by enabling much greater cure rates and facilitating co-vulcanization with general-purpose rubbers like natural rubber and butyl rubber (IIR) [10]. Chlorinated butyl rubber (CIIR) is thought to be a promising material for applications including vibration reduction and sound insulation. Additionally, CIIR offers a high degree of cross-linking flexibility, a quick rate of curing, and sensitive thermal processing [16]. In recent years, research on the use of block or graft copolymers as compatibilizers for immiscible polymer blends has increased. Since it is one of the most simple and efficient ways to generate new high-performance polymeric materials. Generally, appropriately selected graft or block copolymers are chosen that function as "interfacial agents" to lower interfacial tension and enhance interracial adhesion between the immiscible blend components. SBS block copolymers are composed of glassy polystyrene domains connected by polybutadiene segments, which present a two-phase morphology. Glass transition temperature (T_g) of the PS blocks is approximately (+95) °C, whereas the PB blocks' T_g

is approximately (– 80) °C. The PS blocks are glassy and suited to enhance the stiffness of SBS, while the PB blocks are rubbery and can provide elasticity to SBS. This SBS block copolymer is used as Thermoplastic Elastomer (TPE). The special properties of SBS have been well accepted as a compatibilizing agent for rubber blends. The present work is aiming to investigate and evaluate the compatibility of natural rubber with different types of butyl rubbers utilizing different techniques such as: physico-mechanical properties, rheological characteristics, SEM and heat of mixing to examine the compatibility of numerous rubber-rubber blends and namely NR/IIR, NR/BIIR, and NR/CIIR either with or without the presence of styrene-butadiene-styrene block copolymer (SBS) and maleic anhydride MA as compatibilizers. The produced rubber blends would be expected to have good performances.

Materials and Experimental Techniques

Materials

- Natural rubber NR (RSS-1) was supplied by Transport and Engineering Company.
- Butyl rubber: copolymer of isobutylene and isoprene IIR-218; specific gravity 0.92 ± 0.005 ; Mooney viscosity ML (1 + 8) at 125°C 49 ± 2 .
- Bromo-butyl rubber (BIIR 2244): Halogen content 2 wt.%, and Mooney viscosity ML (1 + 8) at 125°C 46 ± 2 .
- Chloro-butyl rubber (CIIR) is a chlorinated butyl rubber with Mooney Viscosity ML (1+8) at 125°C 34, and specific gravity of 0.93.
- Triblock copolymer SBS was from Shell Co., Japan (KRATON D1101).
- Maleic acid anhydride (MA); melting point 52.5°C; boiling point 202°C, and specific gravity 1.48.
- The other rubber ingredients such as; zinc oxide (ZnO) and stearic acid (St. Ac.) (used as accelerator activators), Dioctyl phthalate (DOP) (used as a plasticizer), Zinc Diethyl Dithiocarbamate (ZDEC) (used as an accelerators), elemental sulfur (used as a vulcanizing agent) and High-abrasion furnace black (HAF 303) used as reinforcing filler.

Experimental Techniques

Preparation of rubber compounds

All rubber compounds given in Table 1 with the selected ingredients were prepared on a two-roll mill of 470- mm outer diameter, 24 rev/min. speed of the slow roll, and a gear ratio of 1:1.4. The compounding process was carried out as usual regime for rubber mixing with its ingredients.

Characterizations

Determination of rheometric characteristics

The compounded rubber sheets of thickness of about 5 mm were cut with special die and the

rheometric data were obtained using MDR one Moving Die Rheometer, TA Instruments, New Castle, DE, USA) at $152 \pm 1^\circ\text{C}$.

Equation (1) was used to determine the mismatch factor (M_F) obtained from the rheological data [17].

$$M_F = \left[\frac{1}{(t_{c90} - t_{s2})_A} - \frac{1}{(t_{c90} - t_{s2})_B} \right] \times \frac{1}{[(t_{c90})_A - (t_{c90})_B]} \quad (1)$$

Where: t_{c90} represents time for 90% cure and t_{s2} time for two units rise above minimum torque.

Mechanical tests

The tensile tests were carried out using a universal tensile testing machine (Instron 4466) in accordance with ASTM D 412.

Hardness test

The hardness was determined according to ASTM D2240 using a hardness tester (Durometer) Shore A.

Swelling test

Swelling tests were carried out in toluene following ASTM D471-15.24. Cured rubber pieces of the dimension 10×10 mm were weighed using an electronic digital balance at the accuracy of 0.0001 g and soaked into toluene for 24 h at room temperature, then after dried and weighed. The swelling ratio (Q) is calculated from equation (2).

$$Q, \% = \left[\frac{W_2 - W_1}{W_1} \right] \times 100\% \quad (2)$$

Where: Q is the swelling ratio and W_1 and W_2 are the specimen's weights before and after soaking into toluene, respectively.

The molecular weight between crosslinks (M_c) is calculated using the Flory-Rehner equation

$$M_c = \frac{-\rho_R V_s^2}{\Delta V (1 - \nu_R) + \nu_R + \mu \rho_R^2} \quad (3)$$

Where ρ_R is the density of the rubbers; V_s is the molar volume of the toluene (in this study, being $106.35 \text{ cm}^3/\text{mol}$); V_R is the rubber volume fraction; and μ is the rubber-solvent interaction constant [in this study μ (NR) = 0.393, μ (IIR) = 0.41, μ (BIIR) = 0.6392 and μ (CIIR) = 0.4190].

$$V_R = \frac{1}{1+Q} \quad (4)$$

The crosslink density (ν_d):

$$\nu_d = \frac{1}{2M_c} \quad (5)$$

Morphological characterization

To view the developed microstructure for each individual blend sample, Cryo-fracture surfaces of specimens were sputter coated with a thin layer of gold and then examined for morphological structure through a Quanta 200 F field emission scanning electron microscope (FE-SEM, FEI Co., USA) at an accelerated voltage of 5 kV.

Determination of Compatibility by heat of mixing

Mixing free energy (ΔG_m) is an indication for the compatibility. The increase of mixing free

energy represents an incompatibility with the deterioration. According to the theory of thermodynamics, $\Delta G_m = \Delta H_m - T\Delta S_m$. The free energy of mixing for polymer systems depends on the enthalpy (ΔH_m) because of the low entropy of mixing (ΔS_m). Schneier indicated that the compatibility should be predicted via the calculation of ΔH_m based on the Flory Huggins theory [18]. For two polymer blending systems, ΔH_m can be calculated by equation (6):

$$\Delta H_m = \{X_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \left[\frac{X_2}{(1 - X_2) M_2 \rho_2 + (1 - X_1) M_1 \rho_1} \right]^2 \}^{\frac{1}{2}} \quad (6)$$

Where ΔH_m is the mixing enthalpy (J/mol), X is the mass fraction of the polymer; M is the monomer unit's molecular weight (g/mol), ρ is polymer density (g/cm³) and δ is the solubility parameter of polymer (cal/cm³)^{1/2}. The system is compatible if ΔH_m is $< 41.1853 \times 10^{-3}$ J/mole and incompatible if ΔH_m is $> 41.1853 \times 10^{-3}$ J/mole [19, 20].

Results and discussion

Rheological properties

The rheological behavior of rubber compounds is described using a rheometer. Rheometer data typically provide a clear chart regarding processing parameters, such as the viscosity, scorch time, and optimum cure time of rubber compounds. From Tables 1, 2 & 3 it can be observed that in absence or presence of the compatibilizer, cure time t_{c90} and the scorch time t_{s2} of NR-BIIR blends increase by increasing the BIIR ratio. Minimum torque (M_L) is a measure of viscosity of the unvulcanized blend and considered as indication for its processability. One notes that, in the presence of SBS as compatibilizer, M_L value increased by increasing BIIR content in the blend, suggesting a rise in the rubber compound viscosity. This increase in viscosity is ascribed to the enhanced interfacial interactions between SBS and the BIIR-NR macromolecular chains.

The maximum torque (M_H), which is inversely proportional to the compound's stiffness and modulus, is achieved during the curing test. M_H value increases with increasing NR content in the blend formulations, because NR is higher in stiffness than CIIR, or IIR or BIIR. The value of M_H in presence SBS block copolymer is lower than without compatibilizers. In addition, the SBS employed in the blend may function as a lubricant that is why the maximum torque has decreased [20, 21]. However, the presence of compatibilizers in the NR/IIR, NR/BIIR, and NR/CIIR blends indicated a little decrease in M_H , which may be attributed to the greater dispersion of SBS in the blend formulations with pure rubber. Also, it was observed that the value of M_L of NR/ IIR, NR/BIIR and NR/CIIR compatibilized rubber blends are higher than the

uncompatibilized ones. This may be attributed to the SBS's strong viscoelastic plasticity nature. On the other hand, the M_H of the NR/IIR, NR/BIIR and NR/CIIR blends decreases with the addition of SBS in the blend. This is because the blend has become more polar, which lowers the M_H value. Therefore, the torque difference between M_H and M_L (ΔM) is decreased. It is considered as measure of the cross-link density of the blends. It is seen that torque difference (ΔM) decreases upon adding SBS as compatibilizer, while the crosslink density increases for n NR/IIR, NR/BIIR and NR/CIIR without compatibilizer. However, the declining torque difference for rubber blends suggests that a distribution of cross-links occurred, resulting in an over-crosslinked phase and a less crosslinked phase [22]. From Table 1, it is clear that the value of optimum cure time (t_{90}) for pure IIR, BIIR and CIIR is higher than pure NR. This may be due to the migration of cures to a more unsaturated natural rubber (NR) phase, which is incompatible with these systems (NR/IIR; NR/BIIR and NR/CIIR blends). Viscosity, rubber polarity, and degree of unsaturation are the variables influencing the curative migration. In this research, curative migration occurs from highly unsaturated rubber (NR) to lower unsaturated ones (IIR, BIIR and CIIR) [23, 24]. Beside to the faster cure rate (CRI) in highly unsaturated rubber makes the variance more outstanding. The number of unsaturation in natural rubber (NR) is very high compared to synthetic rubbers butyl (IIR), bromobutyl (BIIR) and chlorobutyl (CIIR) and curing is very fast but these synthetic rubbers takes more time to get cured. Likewise, observed that, in 25/75 NR/IIR, 25/75 NR/BIIR and 25/75 NR/CIIR blend system; the possibility for better migration can occur due to the variation in unsaturation, polarity and viscosity. The incompatibility between these blend systems can reduce the interphase crosslinking that is why increasing the optimum cure time t_{90} . From Table 2, it is noted that after adding CBS as a compatibilizer to the blend systems, decreases the agglomeration which facilitates the crosslinking, reducing the optimum cure time t_{90} . As well from Table 2, it was observed that the presence of SBS compatibilizer in the investigated blends caused an increase in the minimum torque M_L , which enhanced the viscosity of the blends. They explained the increase in viscosity by speculating about possible interactions between NR and SBS. Since the extra viscous blends had higher amounts of molecular tangles, it appears that the increase in M_L is a reflection of greater mechanical work [25]. The NR/IIR blends with MAH/CB (carbon black) system had the longest scorch time, which indicate the harmless processing times as compared to other blends (NR/CIIR and NR/BIIR) with MA/CB (Table

3). Blends will be safe if processed below the scorch time, during which time they can still be created and are still plastic. The plastic material is transformed into chemically elastic according to the t_{s2} scorch time [26]. The effect of the loading of carbon black (CB) and maleic anhydride (MAH) to the NR/IIR blend on minimum torque (M_L) and maximum torque (M_H) is shown in table 3. It has shown that the (M_H) and (M_L) of NR/IIR blends increased with decreasing NR rubber content. This observation was most likely caused by the NR/IIR rubber blend's cross-linking with carbon black and other additives [27, 28], which increased the flow resistance in the rubber blend. The decreasing torque differential between NR/BIIR & NR/CIIR suggests that cross-linking was not distributed evenly [17, 29], leading to an over-cross-linked phase and a poorly cross-linked phase. The isolated double bonds in BIIR and CIIR prevent the formation of intramolecular sulfide linkages, which lowers the rate of cross-linking. On the other hand, the compatibility can be achieved if the surface-energy mismatch between the two components rubber is sufficient to allow the development of very small micro domains of the various polymer phases. The sufficient adhesion between the two phases usually leads to the formation of crosslinks across the interfaces during vulcanization [30]. With respect to NR/IIR, NR/BIIR and NR/CIIR blends, the mismatch factor (Mf) generally provides information about the compatibility of these blends before and after the addition of SBS or MAH/CB as compatibilizers. The values of Mf are less than one as listed in Tables (1, 2 &3). Generally, the smaller the mismatch factor, the stronger rubber to rubber bond is expected [31]. So, the bond strength is a function of the cohesive strength between the two components. From these tables it was observed that the value of Mf decreased for these blend systems in presence SBS compatibilizer. Hence, these blends in presence of the SBS compatibilizer partially increase the interfacial adhesion between the two rubber phases in NR/IIR, NR/BIIR and NR/CIIR blends and also enhanced the rheometric properties. These results were in good agreement with the results of calculated heat of mixing.

Mechanical Properties

Table 4 demonstrated that the uncompatibilized blends of NR/IIR, NR/BIIR and NR/CIIR at ratio (25/75) have a relatively lower tensile strength than pure NR. This can be explained by the ineffective stress transfer between the immiscible blends' phases as a result of the weak interfacial adhesion of the big dispersed particles. The elongation at break is somewhat improved by adding 8 phr of the copolymer SBS (Table 5). The increase in elongation at break (Eb) may be ascribed to the smaller dispersed IIR, BIIR, or CIIR particles

which may have a plasticizing effect, leading to higher E_b values. While the value of tensile strength and modulus was slightly decreased (Tables 4 & 6). Thermoplastic elastomer could be to blame for this. SBS is less expensive and more elastic than NR. As a result, the resistance to tensile stress is not very strong. The markedly increased elongation at break and slightly decreased tensile properties for the compatibilized blend, on the other hand, are due to the finer and partially homogeneous dispersion, slightly improved adhesion between the phases, and a slightly better developed interlayer formed by the compatibilizers [25]. The compatibilizing impact of SBS is due to the ability of butadiene part interacting with NR phase and the styrene part with IIR, BIIR

and CIIR phase. The addition of a third phase SBS (8%) allowed for optimal stress transfer at the interface, significantly improving the characteristics of these blends [17]. This is another indication that there was compatibilization in the NR/IIR/SBS mixtures, which reduced the interfacial tension between the phases and improved the capacity to sustain the stress transfer from the NR matrix.

As can be seen, as NR content was increased, the tensile strength of the blends NR/IIR/SBS, NR/BIIR/SBS, and NR/CIIR/SBS reduced. The reason could be because SBS is a more rigid thermoplastic elastomer than NR and has higher toughness and elasticity. Therefore, the tensile stress resistance is not very strong.

Table 1 Rheometric characteristics of NR/IIR, NR/BIIR, and NR/CIIR Blends without compatibilizer

No. sample/formulation	A	I ₁	I ₂	I ₃	I ₄	B ₁	B ₂	B ₃	B ₄	C ₁	C ₂	C ₃	C ₄
NR	100	75	50	25	--	75	50	25	--	75	50	25	--
IIR	---	25	50	75	100								
BIIR						25	50	75	100				
CIIR										25	50	75	100
Rheometric properties at $\pm 152^\circ\text{C}$													
M_L , dN.m	6	5	4	7	8	7.5	7.75	7.75	10	4	5	6	7.5
M_H , dN.m	46	44	34	26	37	45	42	31	30	43	38	33	28
ΔM , dN.m	40	39	30	19	29	37.5	32.3	23.3	20	39	33	27	20.5
t_{s2} , min.	4.5	3	4	6	10	5	6	6.5	7.5	3.5	3	2.5	2
t_{c90} , min	10	8	8.5	12	25	12.5	12.5	14	17	12	12.5	11	13
CRI, min^{-1}	18.18	20	22.2	16.7	6.7	13.3	15.4	13.3	10.5	11.8	10.5	11.8	9.09
Mismatch factor M_f		-1.722				-0.5376				-0.2727			

Table 2 Rheometric characteristics of NR/IIR, NR/BIIR, and NR/CIIR Blends with compatibilizer (styrene-butadiene-styrene (SBS))

No. sample/formulation	A	I _{1S}	I _{2S}	I _{3S}	I _{4S}	B _{1S}	B _{2S}	B _{3S}	B _{4S}	C _{1S}	C _{2S}	C _{3S}	C _{4S}
NR	100	75	50	25	--	75	50	25	--	75	50	25	--
IIR	---	25	50	75	100								
BIIR						25	50	75	100				
CIIR										25	50	75	100
SBS	8	8	8	8	8	8	8	8	8	8	8	8	8
Rheometric properties at $\pm 152^\circ\text{C}$													
M_L , dN.m	8	7	6	9	10	8.5	9	10	13	6	7	8	9.5
M_H , dN.m	43	41	31	25	39	44	40	37	29	40	31	28	24
ΔM , dN.m	35	34	25	26	29	35.5	31	27	16	34	24	20	14.5
t_{s2} , min.	4	2.5	3	4	7	5.5	7	7.5	8	5	3.5	3	2.5
t_{c90} , min	8	7	8.5	12	20	8.5	9.5	11	15	9	8	10	11
CRI, min^{-1}	25	22.2	18.18	12.5	7.7	33.33	40	28.6	14.3	25	22.2	14.29	11.86
Mismatch factor M_f		-2.076				-0.749				-0.396			

Table 3 Rheometric characteristics of NR/IIR, NR/BIIR, and NR/CIIR Blends with compatibilizer (maleic anhydride (MAH))

No. sample/formulation	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12	M13
NR	100	75	50	25	--	75	50	25	--	75	50	25	--
IIR	---	25	50	75	100								
BIIR						25	50	75	100				
CIIR										25	50	75	100
MA	5	5	5	5	5	5	5	5	5	5	5	5	5
Rheometric properties at $\pm 152^\circ\text{C}$													
M_L , dN.m	1	2	3.5	5.25	7.75	3	4.5	6.5	6.5	2.5	4	6.5	7.5
M_H , dN.m	39	52	48.75	57.2	62.5	48	47	32.5	20	38	37	35.5	29
ΔM , dN.m	38	50	45.25	51.95	54.75	45	42.5	26	13.5	35.5	33	29	21.5
t_{s2} , min.	1.375	1.5	2.44	2.625	2.25	1.125	1.187	1.375	1	1.25	1.188	0.875	1.25
t_{c90} , min	5.75	4.625	8.75	8.75	10.25	5.75	6	6	3	10	9.5	13	7
CRI, min^{-1}	22.85	32	15.84	16.33	12.5	21.62	20.78	21.62	50	11.43	12.03	8.23	17.46
Mismatch factor M_f		0.4658				-0.738				-0.06813			

Base recipe (in phr): NR (natural rubber) 100; IIR (butyl rubber) 100; BIIR (bromobutyl) 100; CIIR (chlorobutyl) 100; ZDEC Zinc Diethyl Dithiocarbamate; 3phr, 1phr phenyl β -naphthyl amine (PBN) stearic acid 1, zinc oxide 5, sulfur 2; M_L , minimum torque; M_H , maximum torque; T_{s2} , scorch time at 2 torque units after minimum; T_{c90} , optimum cure time (at 90% cure); CRI, cure rate index.

Table 4 Physico-mechanical properties of NR/IIR, NR/BIIR, and NR/CIIR blends without compatibilizer

No. Sample/formulation	A	I ₁	I ₂	I ₃	I ₄	B ₁	B ₂	B ₃	B ₄	C ₁	C ₂	C ₃	C ₄
100% Modulus, MPa	1.28	1.87	1.86	1.97	2.26	1.235	1.199	0.98	0.89	1.58	1.35	1.21	1.1
T.S., MPa	17.5	15.76	12.5	8.45	6.89	14.36	12.08	7.25	5.35	13.9	11.9	7.93	5.04
Elongation at break, %	1350	1012	1007	998	840	1366	1023	997	695	1180	1023	787	683
Young's modulus, N/mm ²	1.3	1.55	1.24	0.85	0.44	0.89	0.79	0.69	0.68	0.99	0.99	0.84	0.65
Hardness, Shore A	49	50	52	52	53	47	46	45.5	45	48	47	48	47
Equilibrium swelling (Q), %	312	278	220	205	290	260	231	225	230	298	249	219	205
Volume fraction of rubber: V _r	0.243	0.265	0.313	0.328	0.256	0.278	0.302	0.308	0.303	0.251	0.287	0.313	0.328
Crosslinking density: ν (mol m ⁻³) x 10 ⁵	12.5	15	23	25	9.3	12	9.6	4.71	0.61	13	18	21.4	23
Molecular weight between crosslinking: Mc(g mol ⁻¹)	4014	3318	2209	1981	5357	4125	5189	1061	8220	3825	2847	2327	2130
1/Q	0.32	0.36	0.45	0.49	0.34	0.38	0.43	0.44	0.43	0.34	0.4	0.46	0.49

M-100, modulus at 100% strain; T.S., tensile strength.

Table 5 Physico-mechanical properties of NR/IIR, NR/BIIR, and NR/CIIR blends with compatibilizer (styrene-butadiene-styrene (SBS))

No. sample/formulation	A	I _{1S}	I _{2S}	I _{3S}	I _{4S}	B _{1S}	B _{2S}	B _{3S}	B _{4S}	C _{1S}	C _{2S}	C _{3S}	C _{4S}
M at 100%E, MPa	1.25	1.77	1.8	1.9	2.16	1.145	1.09	0.85	0.79	1.28	1.15	1.11	0.99
T.S., MPa	16.3	13.8	10.1	8.05	5.28	13.36	11.08	7.25	5.35	12.9	10.09	7.13	5.04
Elongation at break, %	1421	1215	1165	1013	860	1406	1088	1007	725	1266	1078	887	708
Young's modulus, N/mm ²	1.14	1.11	0.94	0.63	0.56	0.8	0.74	0.66	0.66	1.3	1.1	0.96	0.76
Hardness, Shore A	44	44.5	45	46	47	46	44	42	40	48	47	46	47
Equilibrium swelling (Q), %	345	336	260	225	250	322	262	212	199	307	293	215	209
volume fraction of rubber: V _r	0.225	0.229	0.278	0.308	0.286	0.237	0.276	0.321	0.334	0.246	0.2544	0.317	0.324
Crosslinking density: ν (mol m ⁻³) x 10 ⁵	10	11	17	21	17	7.88	7.15	5.75	1.004	13	13	22	23
Molecular weight between crosslinking: Mc(g mol ⁻¹)	4827	4702	2996	2346	2905	6344	6992	8686	49786	3896	3847	2249	2208
Qcomp/Qgum	1.11	1.21	1.18	1.1	0.86	1.24	1.13	0.94	0.87	1.03	1.18	0.98	1.02
1/Q	0.29	0.297	0.385	0.44	0.4	0.31	0.382	0.47	0.5	0.33	0.34	0.47	0.48

From Table 6 it is noted that the value of tensile strength of blends NR/IIR/MA/CB is higher than that of NR/BIIR/MAH/CB and NR/CIIR/MAH/CB blends. The polarity difference between the components of the system may be the cause of the reduced efficiency of the BIIR/MA/CB and CIIR/MA/CB blends. This polarity difference did not favor the system (NR/IIR), most likely because none of the rubbers (IIR and NR) have active functional groups that can react with the maleic anhydride (MAH), stabilizing the interface, in their molecular structures [20, 32].

This improvement is the result of the maleic anhydride's interaction with the hydroxyl groups in the filler (CB) through chemical bonds, which would create covalent bonds and ester linkages to strengthen the bonding of the filler matrix, and the NR chain in MAH would melt and form a single phase with the NR matrix.

In sulfur-curative systems, curative migration to the NR phase is superior to that to the CIIR phase. This causes NR to have a greater number of crosslink interfaces, which reduces the time required for optimum cure (t_{90}) in blends with a

larger percentage of NR. From tables (4-6) it was observed that, blends containing MAH/CB gave the highest tensile strength and hardness while the elongation is the lowest. On the other hand, blends containing SBS or without compatibilizers produced blends with the highest elongation and the lowest hardness and tensile strength. Hardness and tensile strength are related to crosslinking density [21, 33]. Higher crosslinking density indicated that the molecules of blend are tight, rigid and hard.

According to Table 4, all mixes (NR/IIR) had values for hardness that were higher than NR. Blends exhibit this characteristic as a result of the IIR rubber compound's incorporation into the NR matrix, which reduces the material's flexibility and raises the Shore D hardness of NR/IIR blends. Additionally, Shore D of NR/IIR/SBS blends decreased in SBS compatibilized blends.

Table 6 Physico-mechanical properties of NR/IIR, NR/BIIR, and NR/CIIR blends with compatibilizer (maleic anhydride (MAH))

No. sample/formulation	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12	M13
M at 100%E, MPa	2.36	2.176	2.09	2.58	2.65	2.8	2.08	1.83	1.81	3.54	2.62	2.59	1.78
T.S., MPa	19.45	22.84	17.8	15.13	17.96	11.98	11.3	12.46	13.5	17.5	10.6	8.34	15.7
Elongation at break, %	500	500	475	400	525	300	375	450	625	350	300	275	500
Young's modulus, N/mm ²	1.77	1.63	1.57	1.94	1.99	2.1	1.56	1.37	1.357	2.66	1.97	1.94	1.34
Hardness, Shore A	55	58	63	63	65	60	64	58	45	57	61	61	51
Equilibrium swelling (Q), %	250	218	215	187	181	168	136	157	195	157	166	143	150
volume fraction of rubber: V _r	0.286	0.314	0.317	0.348	0.356	0.373	0.424	0.389	0.339	0.39	0.376	0.411	0.4
Crosslinking density: $\nu(\text{mol m}^{-3}) \times 10^5$	19	23	24	30	24	28	31	14	1.29	41	37	46	41
Molecular weight between crosslinking: Mc(g mol ⁻¹)	2680	2133	2119	1679	2108	1760	1623	3581	38550	1208	1369	1084	1212
Q _{comp} /Q _{gum}	0.8	0.78	0.98	0.91	0.62	0.65	0.59	0.7	0.85	0.53	0.67	0.65	0.73
1/Q	0.4	0.46	0.47	0.53	0.55	0.6	0.74	0.64	0.51	0.64	0.6	0.7	0.67

M-100, modulus at 100% strain; T.S., tensile strength. Q_{comp}, equilibrium swelling of samples containing compatibilizer; Q_g equilibrium swelling of samples without compatibilizer.

However, blends containing SBS, being a thermoplastic elastomer that without any mineral filler in its composition functioned to soften the surfaces of the compatibilized blends, lowering the penetration resistance when compared to the NR/IIR uncompatibilized blends. While, the values obtained for NR/BIIR and NR/CIIR blends had lower hardness values than NR. This behavior of blends is due to the addition of the BIIR or CIIR rubber compound to the NR matrix, which increases the material's flexibility and lowers its Shore D hardness. According to the works [22, 23], the hardness is attributed to the rubber matrix and the existence of inorganic fillers (such as CB), suggesting that the hardness depends on the surface properties of the blends and, therefore, overlaps the effect of the interfacial adhesion, which explains the different behavior of the NR/IIR/MA/CB, NR/BIIR/MA/CB, and NR/CIIR/MA/CB blends for this particular property. In these blends the inorganic fillers (carbon black) diffused over the blend's surface, enhancing the hardness in comparison to blends that had been compatibilized. Therefore, blends containing MA had the higher values of hardness. The location of CB at

the interface, promotes the formation of continuous morphology in the NR/IIR/MA/CB, NR/BIIR/MA/CB and NR/CIIR/MA/CB blends composite.

Swelling Behavior

The crosslinking density in the rubber matrix is measured by the swelling percentage, and a decrease in swelling corresponds to an increase in crosslinking density. According to Table (4-6), NR/IIR/MA/CB blend vulcanizates have higher crosslinking density values than NR/IIR with and without compatibilizers. This suggests that maleic anhydride /carbon black (MAH/CB) will disperse more effectively when compared to filler in the earlier scenario; this suggests a better distribution of MA/CB. Additionally, the crosslinking density is higher for IIR and CIIR as compared to BIIR, as well as for mix composites combining NR/CIIR/MAH/CB. The characteristics modulus at 100% elongation and equilibrium swelling properties go hand in hand. Additionally, this fits the observed trend in the modulus values derived from the stress-strain data. Rubber CIIR or BIIR without compatibilizer have exhibit the lowest equilibrium

swelling values, while NR has the largest. The reduced solvent absorption of CIIR or BIIR is caused by their higher polarity. As a result, the blends' solvent absorption gradually decreased as their CIIR or BIIR content rose. On the other hand, the nonpolar solvent in the rubber blend has less mobility because of the polar character of CIIR or BIIR. We may infer that combining NR/ CIIR or NR/BIIR increased the resistance to hydrocarbon penetration, making these blends appropriate for uses where the rubber is exposed to a hydrocarbon environment. When comparing uncompatibilized and compatibilized counterparts, the NR/IIR; NR/BIIR and NR/CIIR blends in presence MA/CB compatibilized blends show better solvent resistance. Lower toluene absorption rates for compatibilized blends can be explained with the better interaction between NR/IIR; NR/BIIR and NR/CIIR phase and MA/CB.

The higher swelling ratio ($Q_{\text{comp}}/Q_{\text{gum}}$) value, the lower value would be the amount of interaction between the compatibilizers and investigated rubber blends matrix. The values of $Q_{\text{comp}}/Q_{\text{gum}}$ were calculated using Lorenz and Park's equations [33-35] and listed in Tables (4-6), from which it could be seen that vulcanizate of the lowest $Q_{\text{comp}}/Q_{\text{gum}}$ value and the greatest $1/Q$ was that containing pure IIR/SBS; 25/75 NR/IIR/SBS; pure BIIR; 25/75 NR/BIIR/SBS; pure CIIR/SBS and 25/75 NR/CIIR/SBS blends. Lower value of ($Q_{\text{comp}}/Q_{\text{gum}}$) indicates better interaction between the SBS and the rubber blend matrix. While, in case of MA/CB, it could be seen that vulcanizate of the lowest $Q_{\text{comp}}/Q_{\text{gum}}$ value and the greatest $1/Q$ was that containing pure IIR/MA/CB; 75/25 NR/IIR/MA/CB; 50/50 NR/BIIR/ MA/CB; 75/25 NR/CIIR/MA/CB and 25/75 NR/CIIR/ MA/CB blends. Lower value of ($Q_{\text{comp}}/Q_{\text{gum}}$) indicates better interaction between the MA/CB and the rubber blend matrix at these ratios [36].

Investigation of Blend Morphology

The morphology of NR/Butyl rubber blends was studied by SEM micrographs and is represented

in Fig. 1. The SEM micrographs of NR vulcanizates is displayed in Figure 1(a) was homogeneous, but there is small voids in the matrix. These particles may come from metal oxides (ZnO) used in rubber vulcanization, rubber accelerators, fractures, and slight deformation. According to Fig. 1, all blends exhibited a phase-separated kind of morphology in which IIR, BIIR, and CIIR droplets were scattered throughout the NR matrix. The NR/IIR blend image was shown in Fig. 1(b). Many smooth holes can be seen at the surface of the cry-fractured samples, showing that the interfacial adhesions between the two phases are still insufficient. Due to the reduced interfacial tension and lower viscosity of BIIR and CIIR, the NR blend with BIIR and CIIR, are shown in Fig. 1(c & d), nevertheless, showed fine rubber particles. These two factors are reportedly both quite important.

Fig. 1 (b) to (d) detects the presence of numerous voids, suggesting a low interfacial adhesion among phases, in addition to incompatibility. Additionally, smooth surfaces without any roughness are seen, which supports the idea that the phases adhere poorly to each other's which reduces the stress transmission from the NR matrix to the various IIR particles. The poor mechanical characteristics of this system are confirmed by the incompatibility between NR and IIR phase. However, compared to the uncompatibilized blend, the impacts of the SBS and MA compatibilizer produce different surface properties [29, 30]. Fig. 1 (e) to (j) demonstrates a decrease in the amount of voids in the morphology of the compatibilized blends when comparing the compatibilized blends to the binary blend, which is believed to have a stronger adhesion among blend ingredients. By preventing the formation of agglomerates and stabilizing the morphology of blends, the SBS and MA addition with content of 5% tends to lower the interfacial tension and the amount of voids and delamination. It can be shown that the addition of SBS or MA improved the compatibility of NR with various butyl rubber matrixes. [31].

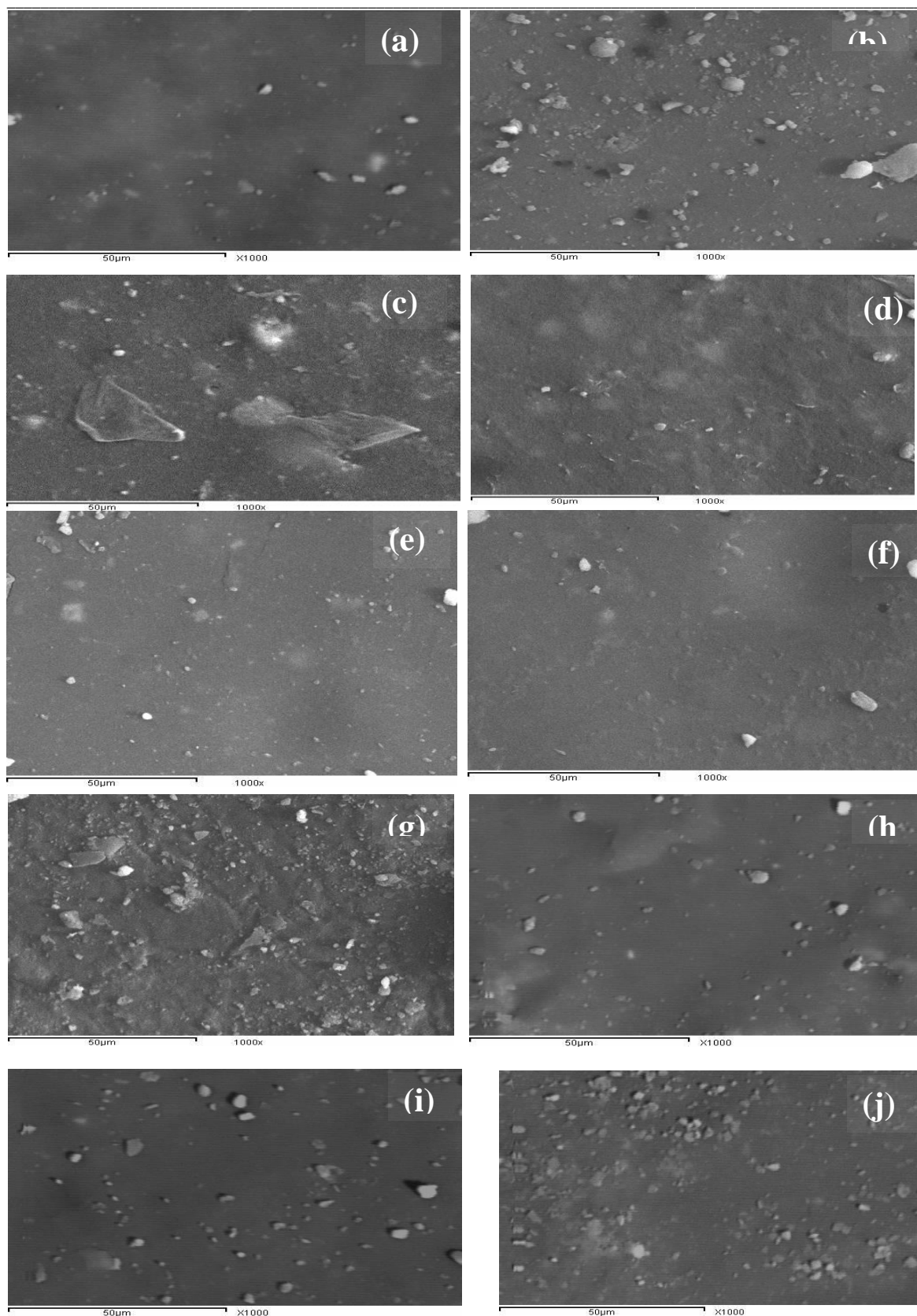


Fig.1. SEM of (a) pure NR, (b) NR/IIR (50/50 phr), (c) NR/BIIR (50/50 phr), (d) NR/CIIR (50/50 phr), (e) NR/IIR/SBS (50/50 phr), (f) NR/BIIR/SBS (50/50 phr), (g) NR/CIIR/SBS (50/50 phr), (h) NR/IIR/ **MAH** (50/50 phr), (i) NR/BIIR/**MAH** (50/50 phr) and (j) NR/CIIR/ **MAH** (50/50 phr)

Thermodynamics of NR/IIR, NR/BIIR and NR/CIIR blends

When the following criterion is met, thermodynamic miscibility and homogeneity can be achieved:

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0 \quad (7)$$

Where these variables are ΔG_m = the Gibb's free energy, ΔH_m = enthalpy and T = temperature and ΔS_m = entropy the sign of ΔG_m is always dependent on the amount of the enthalpy of mixing ΔH_m , which is minimal when two high-molecular-weight polymers are mixed. The degree of homogeneity of NR/IIR, NR/BIIR, and NR/CIIR blends can be assessed by the heat of mixing of such systems. Enthalpy ΔH_m is calculated according to the Schneier equation [18, 26]. The system is compatible if ΔH_m is $< 41.1853 \times 10^{-3}$ J/mole and incompatible if ΔH_m is $> 41.1853 \times 10^{-3}$ J/mole [26, 27]. Due to the poor adhesion between the phases, the resulting products of incompatible rubber mixtures frequently have poor mechanical properties. To decrease phase separation and promote interfacial adhesion, experiments have been done with the addition of physical or chemical compatibilizers [18, 26], a third polymer or graft or block copolymer that joins with the two phases, and the introduction of covalent connections between the polymer phases. The results of rheological and mechanical testing were compared, and the heat of polymer-polymer blend mixing was determined. Using the Schneier equation [33], Singh and Singh [29] calculated the heat of mixing of some polymer blends over the full range of compound and weight fraction in blends and it is understood that heat of mixing values below 41.1853×10^{-3} J/mole indicate complete compatibility of blends, while the incompatible blends have mostly higher values. Since the heat of mixing for NR/IIR; NR/BIIR and NR/CIIR mixes are above the top limit of compatibility (41.1853×10^{-3} J/mole), it is expected from Fig.2 that they are thermodynamically incompatible. In other words, the NR/IIR; NR/BIIR and NR/CIIR blend mixes in these systems exhibit phase separation. The heat of mixing values of these blend systems are 389×10^{-3} ; 256×10^{-3} and 193×10^{-3} J/mole respectively (as shown in Table 7). These values are higher than the upper limit compatibility. This reveals the presence of weaker intermolecular interaction between the unlike segments of the component in the binary rubber mixture. This will also support the presence of weaker intermolecular hydrogen bonding in the binary rubber blends. Trials were conducted to improve the compatibility of this system in order to solve the phase separation issue.

It may be simple to increase the compatibility of NR/IIR; NR/BIIR and NR/CIIR rubber blends that are intrinsically incompatible with one another by adding a different component that is compatible with these blends and is preferably situated at the interface between the two phases in NR/IIR; NR/BIIR and NR/CIIR blends. In order to improve the compatibility of the aforementioned binary rubber mixes, compatibilizing agents such as maleic anhydride (MAH) and styrene-butadiene-styrene (SBS) were utilized. Based on Fig.2, when these compatibilizers are added to the NR/IIR; NR/BIIR and NR/CIIR blend systems, the heat of mixing value was significantly higher than the compatibility upper limit. These findings unambiguously show that the inclusion of the examined compatibilizers enhances the interaction between the phases and consequently slows the phase separation process, [23]. These thermodynamic calculations may imply a substantial degree of compatibility; this compatibility leads to intermolecular diffusion over the interface [23], which was corroborated with results of rheometric, SEM, and mechanical characteristics. Note that, upon addition of SBS or MA as compatibilizers to the investigated blends the maximum value of heat of mixing was decreased as compared to those without compatibilizers. It follows that the compatibility between rubber matrix and CB has been enhanced and that these compatibilizers (SBS & MA) have also been successful in acting as a coupling agent between rubber blend matrix and CB. As a result, the compatibility between rubber matrix and CB has improved, and these compatibilizers (SBS & MA) have also been effective in functioning as a coupling agent between rubber mix matrix and CB (as represents from data in Table 7). These findings demonstrate that the inclusion of the tested compatibilizers enhances phase interaction, delaying phase separation [23]. This level of compatibility, which facilitates intermolecular diffusion across the interface, may be strongly suggested by these thermodynamic calculations, which is corroborated by results from rheometric, SEM, and mechanical characteristics [32, 37].

Table 7 Maximum value of heat of mixing for the investigated blends

Type of blend	In absence of compatibilizer	In presence of SBS	In presence of MAH
	Maximum value of heat of mixing		
NR/IIR	389×10^{-3} J/mole	50.05×10^{-3} J/mole	52.5×10^{-3} J/mole
NR/BIIR	256×10^{-3} J/mole	63×10^{-3} J/mole	75.9×10^{-3} J/mole
NR/CIIR	193×10^{-3} J/mole	114.8×10^{-3} J/mole	91.8×10^{-3} J/mole

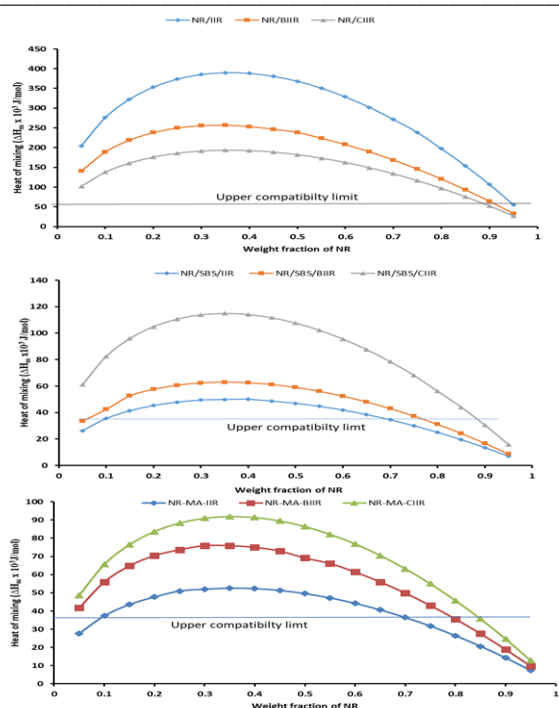


Fig.2. The relationship between the heat of mixing and the weight fraction of NR in absence and in presence of compatibilizers (SBS and MA)

Conclusion

NR/IIR, NR/BIIR, and NR/CIIR rubber blends exhibit macro-phase separation and are incompatible. The addition of compatibilizer lowered the extent of phase separation and increased the interfacial adhesion between phases, consequently decreased the size of the dispersed phase domains. In the presence of (SBS) compatibilizer, the rheometric characteristics of these blends were enhanced as a result of improvement of the interfacial adhesion between the two rubbers phases in NR/IIR, NR/BIIR and NR/CIIR blends. It is evident that as NR content was increased, tensile strength of the prepared blends was reduced. On the other hand, in presence MA/CB system the tensile strength and Young's modulus of these blends increased by decreasing the NR content in the blends. However, the elongation at break enhanced with increasing content of NR in the blends. The anhydride group is expected to be appropriately reactive with the hydroxyl groups of carbon black filler and serve as a bridge between the filler and the rubber polymer matrix. The maximum value heat of mixing was decreased after adding SBS or MA as compatibilizer to the blends. In other words, compatible blends show better interface adhesion, which led to improving the compatibility between rubber components at the micro scale, and hence, enhancement in the mechanical properties can be noted. All blends achieve partial compatibility after the addition of the compatibilizers MA/CB

and SBS, which is supported by swelling behavior and estimated heat of mixing.

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