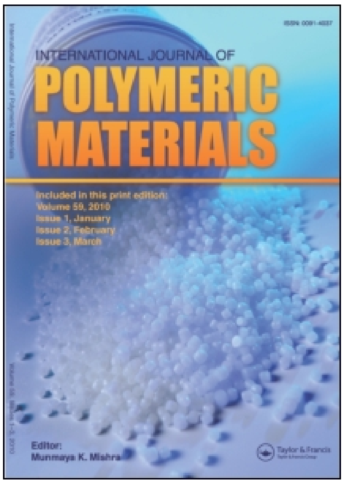

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Elastic Behavior of NR/IIR Rubber Blend Loaded with Different Compatibilizers

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The effect of the addition of different compatibilizers such as bromobutyl rubber (BIIR) and maleic anhydride (MA) on the elastic behavior of natural rubber/butyl butyl rubber (NR/IIR) blend has been studied by carrying out equilibrium stress-strain measurements for these blends. From the stress-strain curves, Young's modulus was found to have a maximum value at around 5 phr of BIIR and two maxima were observed at 2 and 12.5 phr of maleic anhydride. The modified Mooney-Rivlin equation was used to calculate the parameters C_1 and C_2. The Song et al. model was tested here to fit the stress-strain curves at both small and large strain, which is capable of accurately describing the mechanical behavior of these blends.

Keywords: bromobutyl, compatibilizers, maleic anhydride, natural and butyl rubber, rubber blend

INTRODUCTION

The unique versatility of rubber has never before been manifested so acutely as in the development of conducting rubber, a class of materials that is traditionally well known and widely used as insulator [1].

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The importance of polymer blends and composites is largely due to the fact that such low density materials can have unusually high elastic moduli and tensile strength [2–5]. For the most part, the tensile properties have been quite adequately dealt with by utilizing the theory of elasticity. The molecular theory of rubber elasticity developed by Flory and Erman [6–9] is based on the idea of constrictions imposed by entangled network chains on crosslink fluctuations. For developing a quantitative physical basis for the stiffness and the strength of vulcanizates composites, they have been studied by dealing with the elastic behavior [10]. Analysis of stress-strain data obtained from rubber is based on the formula [10].

$$\mathrm{E} = \mathrm{E}_0(1 + 2.5\ \mathrm{C}) \tag{1}$$

where E is the Young's modulus of the rubber composite, E_0 is the modulus of the matrix, and C is volume fraction of the filler.

The classical kinetic theory developed by Wall [11], Flory [12] and James and Guth [13] attributed the high elasticity of a crosslinked rubber to the change of the conformational entropy of the long flexible molecular chains. The theory predicts the relation:

$$\sigma = \mathrm{A}\upsilon\ \mathrm{k}\ \mathrm{T}(\lambda^2 - \lambda^{-1}) \tag{2}$$

where σ is the true stress, υ is the number of effective elastic chains per unit volume, k is the Boltzman's constant, T is the absolute temperature, λ is the extension ratio, and A is a pre-factor, depending on the considered model.

The blending of rubbers depends greatly on the adhesion between the different rubber phases. Several trials were carried out to minimize the phase separation and increase interfacial adhesion; these included the addition of physical or chemical compatibilizers [14,15] (the addition of a third homopolymer or graft or block copolymer) that bind with the two phases, and the introduction of covalent bonds between the homopolymer phases.

Following a series of work, [16,17] aiming to study the compatibility of polymer blend systems by electrical and mechanical techniques, the tensile stress-strain curve is one of the basic characteristics for rubber blends. However, the stress-strain curve contains additional information about rubber properties. The effect of the, type and concentrations of compatibilizer on the mechanical behavior of natural rubber and butyl rubber (NR and IIR) blends will be studied. Moreover, a quantitative analysis of the stress-strain behavior will be elucidated on the basis of empirical models.

EXPERIMENTAL WORK

Materials

Rubber

- **Natural rubber**: Ribbed smoked sheets (RSS-1) with specific gravity 0.913, Mooney viscosity M_L (1 + 4), 60–90 at 100°C & $T_g - 75$°C.
- **Butyl rubber**: copolymer of isobutylene and isoprene IIR-218 specific gravity 0.92 ± 0.005, Mooney viscosity M_L (1 + 8) at 125°C 49 ± 2.

Compatibilizers

- **Bromobutyl rubber** (BIIR 2244), Halogen content 2% weight, Mooney viscosity M_L (1 + 8) at 125°C 46 ± 2.
- **Maleic anhydride**; m.p. 52.5°C, b.p. 202°C, specific gravity 1.48. Compounding ingredients: These are of commercial grades used in industry.
- **All materials** used were supplied by the Transport and Engineering Company (TRENCO, Alexandria, Egypt) (as illustrated in Table 1).

Techniques

Blending of the components was achieved by mastication on a two-roll mill for 5 min, then each blend was mixed in a Brabender plasticorder at a rotor speed of 70 rpm for 5 min. The mixing temperature was 150°C. Then the compatibilizer was added in amounts of 2, 5, 7.5, 10, 12.5 parts per hundred parts of rubber by weight (phr). Then the rubber was mixed with ingredients according to ASTM (D15-72) and careful control of temperature, nip gap and sequenced addition of ingredients. Table 1 lists all ingredients of the blend composition

TABLE 1 Formulations,* Characteristics and Mechanical Properties of (50/50) NR/IIR Blend Without Compatibilizers

Ingredients (phr)	S_3
NR	50
IIR	50
Rheometric characteristics at 152 ± 1°C	
M_L (minimum torque) dN · m	4
M_H (maximum torque) dN · m	37
T_{s2} (scorch time), min	3.75
T_{c90} (optimum cure time), min	11
CRI, (Cure rate index) min^{-1}	13.79

*Base recipe (in phr): (NR) nature rubber 50, (IIR) butyl rubber 50, stearic acid 1.5, zinc oxide 5, oil; 3, HAF; 20, N-isorpropyl-N-phenyl-p-phenylebe diamine (IPPD); 1, N-cyclochexyl-2-benzothiazole sulphonamide (CBS) 0.8, sulfur 2.

according to the sequence of their addition During time was deduced using a Monsanto Rheometer at 152 ± 1°C.

Vulcanization was carried out in an electrically heated auto-controlled hydraulic press at 142 ± 1°C and pressure 4 MPa. The compounded rubber and vulcanizates were tested according to standard methods, namely:

a) ASTM D2084-95 (1994) for determination of rheometric characteristic using a Monsanto Rheometer model 100.
b) ASTM D412-8a (1998) for determination of physico-mechanical properties using a Zwick tensile testing machine (model 1425).
c) Hardness was determined according to ASTM D 2240-97 (1997).
d) Fatigue was determined according to ASTM 3629 (1998).

RESULTS AND DISCUSSION

The stress-strain curves of the (50/50) natural (NR)/butyl (IIR) blend compatibilized by different ratios of maleic anhydride (MA) and bromobutyl (BIIR) are shown in Figures 1 and 2 respectively. At strain

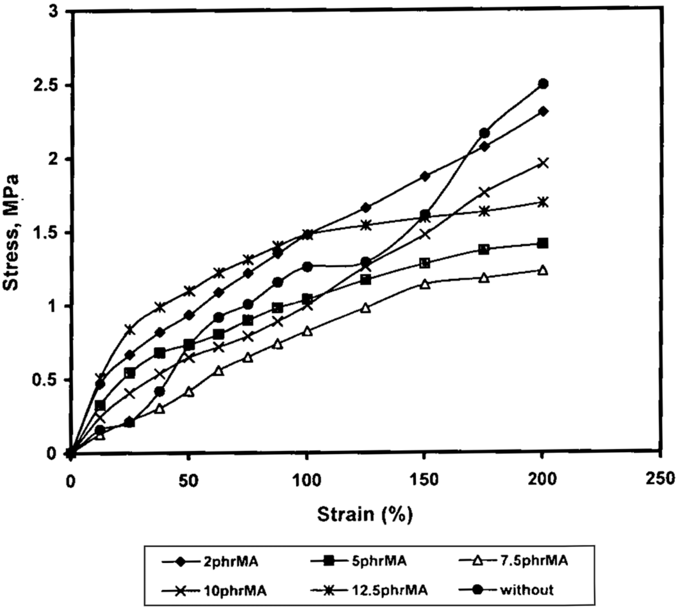


FIGURE 1 Stress-strain curves for (50/50) NR/IIR without and with different ratios of compatibilizer MA.

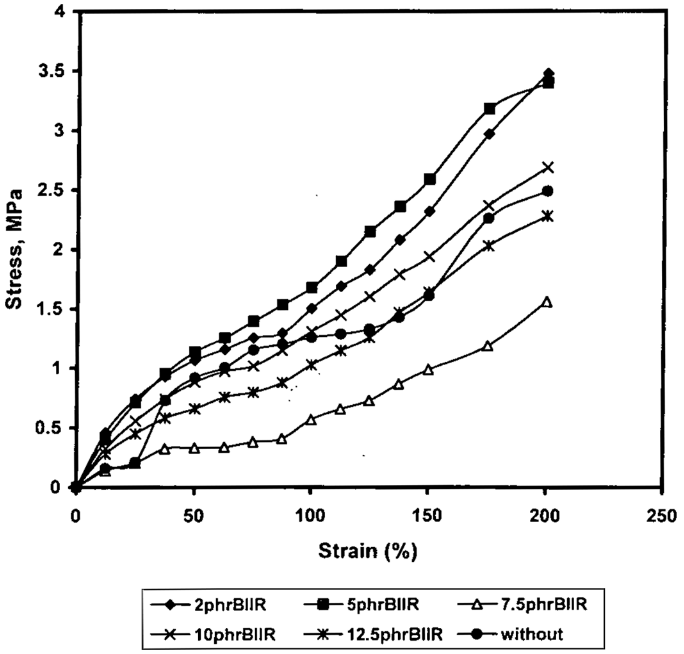


FIGURE 2 Stress-strain curves for (50/50) NR/IIR without and with different ratios of compatibilizer BIIR.

lower than ≈20%, the kinetic theory holds. At larger deformations there is limited extensibility of the crosslinked chains. However, there is a stress-softening effect at moderate strains, especially for higher loaded samples with MA compatibilizer. The linear portions (at low extension) of the curves illustrated in Figures 1 and 2 are used to estimate the values of Young's modulus E, which are shown in Table 2 as a function

TABLE 2 The Value of Young's Modulus

Ratio of Compatibilizer in phr	Young's modulus for BIIR, N/mm^2	Young's modulus for MA, N/mm^2
Without (zero)	1.48	1.48
2 phr	2.89	2.589
5 phr	3.204	1.88
7.5 phr	0.818	1.35
10 phr	2.03	1.875
12.5 phr	1.813	2.97

of both maleic anhydride (MA) and bromobutyl (BIIR) compatibilizers. It is clear from Table 2 that Young's modulus has a maximum value at 5 phr BIIR contents, meanwhile, two maxima is observed for Young's modulus (at 2 and 12.5 phr) in the case of MA compatibilizer indicating the reinforcement properties of MA at these concentrations.

It has been shown by Rivlin et al. [18] that the stress-strain behavior of rubber vulcanizates can be described by the Mooney-Rivlin [19] relation which, in simple extension, gives:

$$\sigma/2(\lambda - \lambda^{-2}) = C_1 + C_2\lambda^{-1} \tag{3}$$

where σ is the true stress, which produces an extension ratio λ in the sample, and C_1 and C_2 are parameters characteristics of the rubber vulcanizate. It has been shown that [19] C_1 is a quantity pertaining to the ideal elastic behavior, while C_2 express the departure from the ideal elastic behavior.

Figures 3(a) and (b) show the experimental stress-strain curves given in Figures 1 and 2 replotted in the forms $\sigma/2(\lambda - \lambda^{-2})$ vs. λ^{-1}.

A limited linear part of stress-strain curves may be utilized to find C_1 from the intercept with the ordinate and C_2 from the slope. However, this situation may be dealt with as follows.

The tendency of increasing compatibility between NR and IIR is achieved at 2 and 5 phr of both MA and BIIR and the strain amplification factor is defined as:

$$X = \sigma/\varepsilon\ E_0 = E/E_0 \tag{4}$$

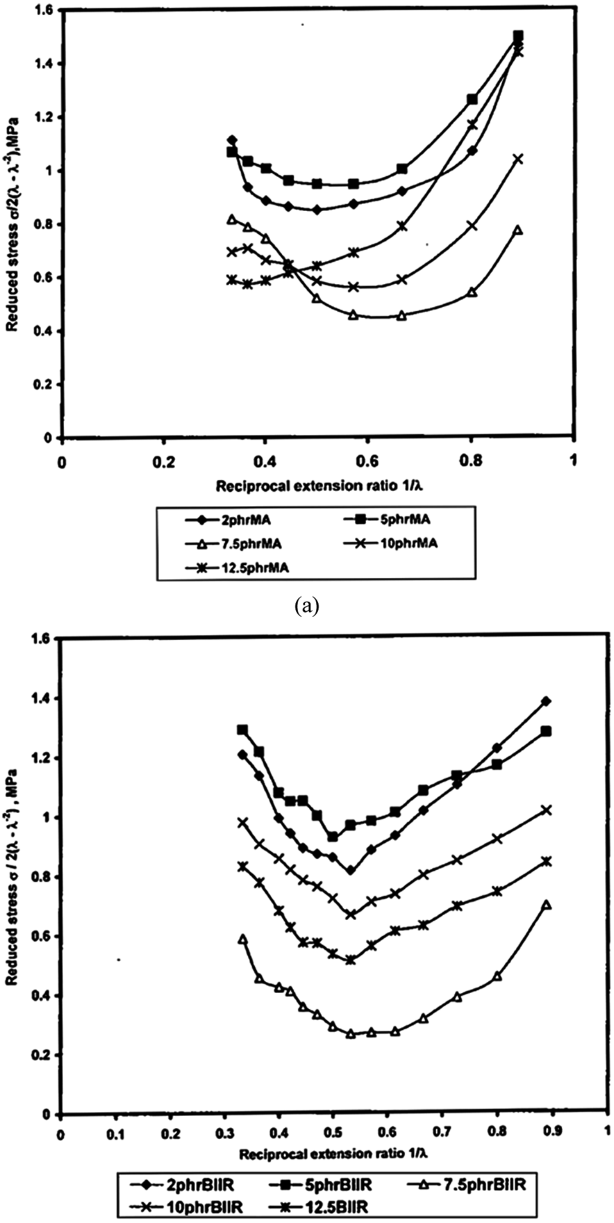
where ε is the strain produced by a stress σ, and E_0 is the modulus of the matrix, meaning that the local strains are on the average X times greater than the overall strains. So the extension ratio Λ in Eq. (3) is replaced [19] by $\Lambda = 1 + X\,\varepsilon$.

Knowing the strain amplification factor given by Eq. (4), the curves of Figures 3(a) and (b) are replotted in Figures 4(a–b) as:

$$\sigma/2(\Lambda - \Lambda^{-2})\ \text{Vs.}\ \Lambda^{-1}$$

in the range of low strains. From these plots the constants C_1 and C_2 are readily determined, and their dependence on the concentration of MA and BIIR is shown in Table 3.

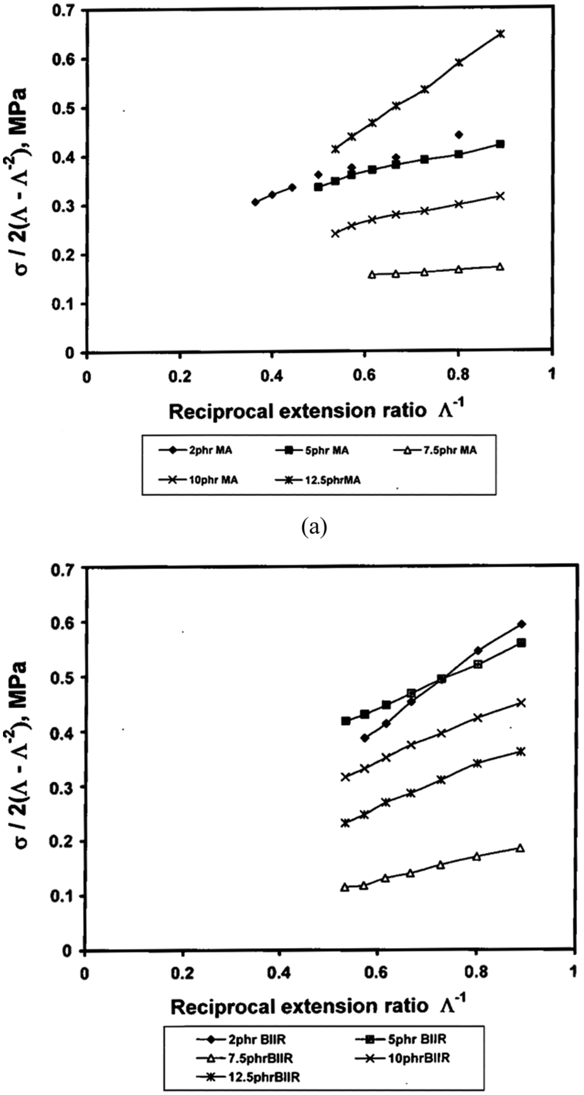
The constant C_1 describes the behavior predicted by the statistical theory of rubber-like elasticity, and its value is directly proportional to the number of network chains per unit volume of the rubber [20]. The value of C_2 determines the number of steric obstructions and the number of effectively trapped elastic entanglements as well as other network defects [21].



(a)

(b)

FIGURE 3 a) Mooney-Rivlin coordinates for (50/50) NR/IIR compatibilized with different ratios of MA; b) Mooney-Rivlin coordinates for (50/50) NR/IIR IIR compatibilized with different ratios of BIIR.



(a)

(b)

FIGURE 4 a) The relation between reciprocal extension ratio $1/\Lambda$ and $\sigma/2(\Lambda - \Lambda^{-2})$ for 50/50 NR/IIR compatibilized with MA; b) The relation between reciprocal extension ratio $1/\Lambda$ and $\sigma/2(\Lambda - \Lambda^{-2})$ for 50/50 NR/IIR compatibilized with BIIR.

TABLE 3 The Value of Constant C_1 and C_2 for Different Ratios of Compatibilizers

Ratio of compatibilizers in phr	C_1 for BIIR (MPa)	C_2 for BIIR (MPa)	C_1 for MA (MPa)	C_2 for MA (MPa)
2 phr	0.84	6.6	2.029	2.966
5 phr	1.46	4.052	2.38	2.066
7.5 phr	0.325	0.206	1.219	0.536
10 phr	1.28	4.05	1.4	1.95
12.5 phr	0.139	4.088	0.828	6.53

The undulatory behavior of both C_1 and C_2 and Young's modulus (as observed in Tables 2 and 3) with both compatibilizers BIIR and MA may be due to the competition between increase and decrease of the number of network crosslinks, steric obstructions and other network defects.

From the Moony-Rivlin plot the elongation inducing the stress upturn is due to the limited extensibility of chains and it increases with decreasing degree of vulcanization and with increasing compatibilizer contents above 2 and 5 phr of both MA and BIIR respectively.

Empirical models other than Moony-Rivlin have also been used to describe the mechanical properties of polymer at various strain rates and over the entire range of measurements.

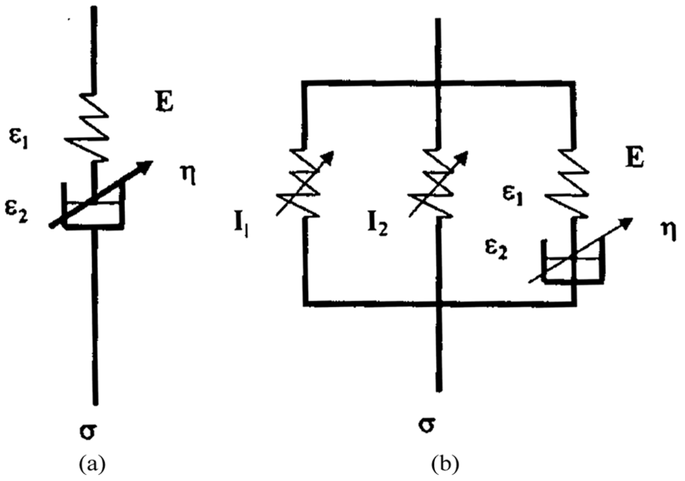


FIGURE 5 a) Maxwell model with a nonlinear dashpot; b) Strain-rate-independent base model.

TABLE 4 The Value of D_0 for MA and BIIR

Ratio of compatibilizer	D_0 (MA)	D_0 (BIIR)
2	4.058	1.68
5	4.76	2.92
7.5	2.438	0.65
10	2.8	2.56
12.5	1.656	0.278

A strain-rate independent stress-strain behavior of polymer at both small and large strains can be expressed according to the Song et al. [22] model with true terms as follows:

$$\sigma = 2\ \mathrm{C}_1(\lambda^2 - \lambda^{-1}) + 2\ \mathrm{C}_2(\lambda - \lambda^{-2}) + \sigma_\mathrm{r}(1 - \mathrm{e}^{-\varepsilon/\varepsilon\mathrm{r}}) \tag{5}$$

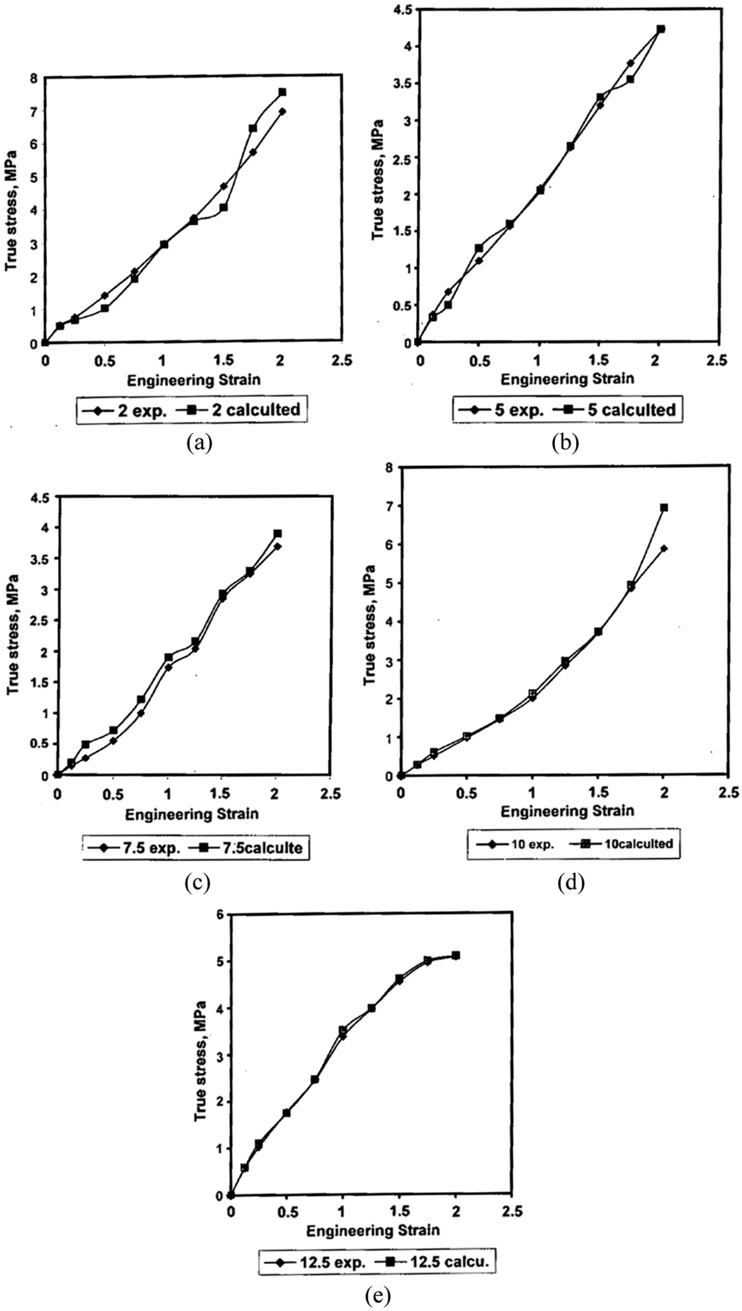
where ε_r is a constant strain rate. Equation (5) can be represented by an illustrative model as shown in Figure 5. Equation (5) represents the base model for the NR/IIR blend, which is composed of a simple strain-energy function (first two terms on the right) and a modified Maxwell model (the last term). The modified Maxwell component describes stress-strain behavior at small strains and will be a constant at large strains where the strain energy function dominates. After cross-examining Eq. 5 by Song et al. [22] with their experimental results for the EPDM rubber in either extension or compression, they devised an expression describing the strain-rate-dependent model for the EPDM rubber of the form:

$$\begin{aligned}\sigma = {} & \mathrm{D}_0[(1+\varepsilon)^2 - (1+\varepsilon)^{-1}] + [\mathrm{A}_0 + \mathrm{A}_1(\acute{\varepsilon}/\acute{\varepsilon}_0)^{\alpha}_{1}] \\ & \times [(1+\varepsilon) - (1+\varepsilon)^{-2}] + [\mathrm{B}_0 + \mathrm{B}_1(\acute{\varepsilon}/\acute{\varepsilon}_0)^{\alpha}_{2}] \times [1 - \mathrm{e}^{-(\varepsilon/\varepsilon\mathrm{r})}]\end{aligned} \tag{6}$$

where $\mathrm{D}_0 = 2\ \mathrm{C}_1$, A_0, A_1, B_0 and B_1 are material constants to be determined experimentally, $\acute{\varepsilon}_0$ is the reference strain rate, α_1 and α_2 are also material constants. The material constants for Eq. 6 are tabulated in Tables 4 and 5 as taken from Song et al. Eq. (6) and tested here for NR/IIR blend loaded with different concentrations of MA and BIIR compatibilizers as shown in Figures 6(a–e) and 7(a–e). The good agreement between Song et al.'s model and our experimental

TABLE 5 Material Constants in Eq. (6)

Constant	A_0	A_1	B_0	B_1	α_1	α_2	ε_r	$\acute{\varepsilon}_0$
Tension	-8.0	0.06269	3.30	-6.32×10^{-6}	0.3502	1	0.18	0.18



(a)

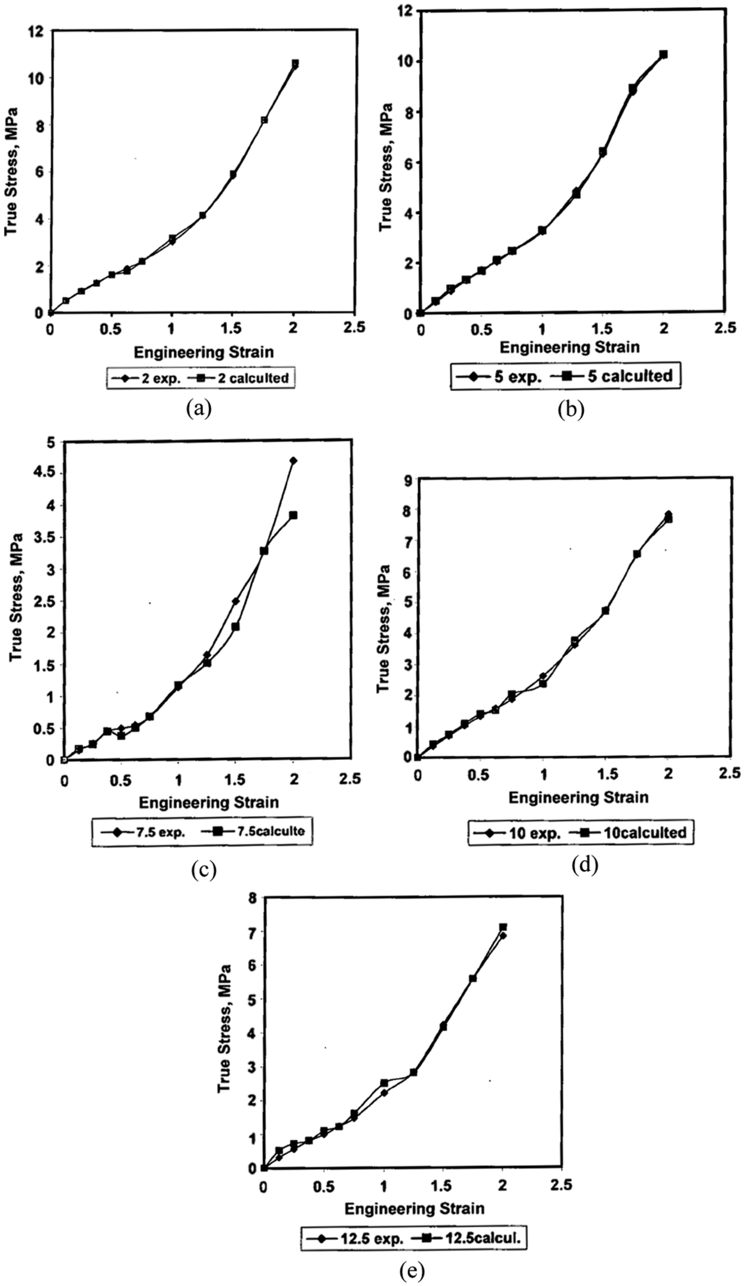
(b)

(c)

(d)

(e)

FIGURE 6 (a–e) Comparison between calculated and experimental values of true stress versus engineering strain for (50/50) NR/IIR compatibilized with different ratios of MA.



(a) (b) (c) (d) (e)

FIGURE 7 (a–e) Comparison between calculated and experimental values of true stress versus engineering strain curves for (50/50) NR/IIR compatibilized with different ratios of BIIR.

results under tensile loading indicates that this model is capable of accurately describing the strain-rate dependent mechanical behavior of rubber blends under tensile loading with small variations of D_0, which has a maximum value at 5 phr of MA and two maxima at 5 and 10 phr, or decreases with MA and (or bromobutyl BIIR) compatibilizer loadings which is in consistence with the change of E according to these loadings.

CONCLUSIONS

From the stress-strain measurements, it was concluded that the mechanical properties of NR/IIR blend have been improved by the addition of 5 phr and 2 phr of MA and BIIR compatibilizers owing to the good compatibility between NR and IIR rubbers. MA and BIIR also affect the values of Cl and C2 as calculated using the Mooney-Rivlin equation, as well as Young's modulus. The Song et al. model was tested here and found to fit well the stress-strain curves at small and large strains for all blend samples.

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