Mechanical Properties of Acrylonitrile butadiene/ Ethylene Propylene Diene Monomer Blends: Effects of Blend Ratio and Filler Addition

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Abstract: Blends based on acrtlonitrile butadiene rubber (NBR) and ethylene propylene diene monomer (EPDM) rubber was prepared with different fast extrusion furnace black (FEF) concentrations. The effect of blend ratio and FEF contents on the mechanical properties, such as stress-strain behavior, tensile strength and elongation at break have been investigated. Tensile and elongation at break showed synergism for the blend containing zero NBR/100EPDM and 80 phr FEF-content. The experimental data have been compared with the relevant theoretical models.
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Keywords: NBR; EPDM; Rubber blend; mechanical properties

1. Introduction

There is great industrial interest in polymer blends since blending is a relatively simple way to create material with significantly improved properties. The properties of polymer blends are closely related to the number, shape and morphology of the dispersed phase particles [1-6]. Fillers, either powders or fibers, are introduced into a broad range of polymers to modify their mechanical properties, thus giving them new application and commercial value [7]. In recent years, the production of elastomeric blends has markedly increased, due to their well- balanced physical and mechanical properties, easy process ability and relatively low cost. Blending of two or more types of polymers is a very useful technique for the preparation and development of materials with properties superior to those of individual constituents [8]. Mechanical properties of blends are mainly determined by the component properties, phase morphology and adhesion between the phases. The phase morphology is dependent on processing factors such as type of mixer, blending rate, blending temperature, component rheology, interfacial tension and cross-linking agent.

Particulate fillers can increase the strength of an amorphous rubber more than 10-fold [9]. For a filler to cause significant reinforcement, it must possess high specific surface area, i.e., the particles must be small, less than 1 μm in size [10]. Small particles have large surface area to interact with the rubber and close particle-to-particle spacing in the compound. Two types of fillers that are most effective for reinforcing rubber are carbon black and silica. They can be produced with a primary size as small as 10 nm, corresponding to a surface area if a few hundred m^2/ gm of filler. The reinforcement of rubber properties by the incorporation of carbon black is due to the presence of active polar groups such as phenol, carboxyl, quinone and lactones on the carbon black surfaces [11- 13]. These polar groups on the carbon black surfaces interact with rubber and the interaction is higher with polar rubbers than hydrocarbon rubbers, which is due to polar- polar interaction [14]. The degree of reinforcement of the filled rubber depend mainly on the filler concentration and principal properties of carbon black such as particle size, surface area, aggregate structure and its distribution in rubber matrix as well as rubber-filler interaction [15].

Blends based on non-polar ethylene-propylene-diene monomer (EPDM) and polar acrylonitrile butadiene rubber (NBR) was prepared and FEF carbon black was introduced through these blends. The interaction between the hydrocarbon rubber and carbon black can be improved by the introduction of polar groups in the rubber through blending or adding some particular additives [16].

This paper describes recent investigations that carried out on the mechanical properties of NBR/EPDM blend filled by (fast extrusion furnace) FEF carbon black. The degree of crooslinking density for prepared compounds was determined. Mechanical properties of an elastomer depend strongly on crosslink density. Modulus increase monotonically with increasing crosslink density and the material becomes more elastic, or stated alternatively, less hysteretic. Fracture properties, such as tear and tensile strength, pass through a maximum as crooslinking is increased. An attempt

has been also made to correlate the mechanical properties with the existing theoretical models.

2. Experimental

2.1 Materials

Ethylene-propylene-diene monomer EPDM (EP35) had propylene content 43wt% and Acrylonitrile butadiene co-polymer rubber (NBR, Nipol) were supplied by Japan Synthetic Rubber Co., Ltd. Fast extrusion furnace FEF N550 carbon black CB, cure activators (zinc oxide and stearic acid) and curatives system based on sulphur were supplied by Transport and Engineering Co. (TRENCO), Alex., Egypt. The basic characteristics of EPDM, NBR and FEF are given in Table (1).

Table (1): Rubbers and carbon black characteristics

Material	Parameter	
Ethylene-propylene-diene monomer (EPDM)	Propylene content (%)	43
	Density (g/ cc)	0.86
	Mooney viscosity (ML_1+4; 100^{0}C)	83
	Volatile material (%)	0.5
	Ashes (%)	0.2
Acrylonitrile butadiene rubber (NBR, Nipol)	Acrylonitrile content (%)	33
	Density (g/ cc)	0.98
	Mooney viscosity (ML_1+4; 100^{0}C)	77.5
	Volatile material (%)	0.75
	Ashes (%)	0.5
Carbon black FEF (N550)	Average Particle Diameter (nm)	43
	N_2 Surface area (m^2/g)	42
	Iodine adsorption (mg/g)	44
	DBP[a] absorption (cm^3/100g)	115
	Ash content (%)	0.2
	Pour Density (g/cc)	0.38

a) Dibutyl Phthalate.

2.2 Sample preparation

EPDM / NBR conductive blends were prepared by the master batch technique. The blend compositions are [0/100, 75/25, 50/50, 25/75 and 100/0 respectively. Rubber blends with a different blend ratios of NBR and EPDM were prepared by mastication of each type then mixing for a period of 20 min. with different ingredients in phr (part per hundred parts of rubber by weight). Compounding was done on two – roll mixing mill (Friction ratio 1:4), according to ASTMD 15-627. After rubber mastication, the compound ingredients such as activators, FEF carbon black, processing oil, accelerators and sulpher were then added constituents in ratios as shown in Table (2). After compounding, the stocks were left for 24 h to mature. It was then cured into sheets of 2mm thick using hot press at 5 MPa pressure and heating temperature 145± 2^{0}C for 20 min. To insure reproducibility, the samples were conditioned at 70°C for 20 days [17].

Table (2): Composition of NBR- EPDM of different blend ratios:

Ingredients (phr)	NBR/EPDM: 100/ 0	NBR/EPDM: 75/ 25	NBR/EPDM: 50/ 50	NBR/EPDM: 25/ 75	NBR/EPDM: 0/ 100
EPDM	0	25	50	75	100
NBR	100	75	50	25	0
Stearic acid	2				
ZnO	5				
Oil	10				
FEF	0, 10, 40, 50 and 80				
MBTS[a]	2				
P N[b]	1				
Sulfur	2				

a) Dibenthazyl disulfide
b) Phynyl- - napthylamine

2. 3 Mechanical property measurements

The mechanical tests were carried out at 27^{0}C by using a home- made universal testing machine with a crosshead speed of 500 mm/min. Rubber composite samples were cut with a die into dog-bone shape of initial dimensions 40 mm in length, 4 mm in width and 2 mm in thickness. The recorded value for each mechanical parameter is the average of three measurements.

3. Results and Discussion

3.1 Stress- strain behavior

The influence of filler content on the mechanical properties of reinforced-elastomers has been extensively reported in the literature [18]. In this work, NBR/EPDM different blend ratios were reinforced with FEF black. The degree of reinforcement usually increases with filler loading. The degree of reinforcement will depend on the extent of polymer filler interaction and the degree of wetting of filler particles by the polymer matrix [19]. The stress- strain curves of different blend compositions as a function of FEF- loading are given in Figures (1- 5). It can be seen that EPDM pure sample loaded with different FEF content withstand stress more.

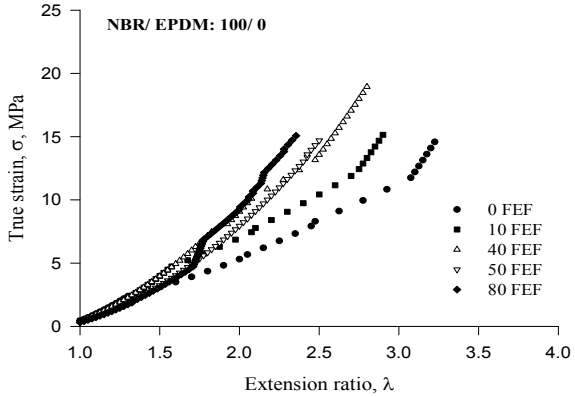

Fig. 1: Tensile stress- strain curves for FEF/ NBR composites

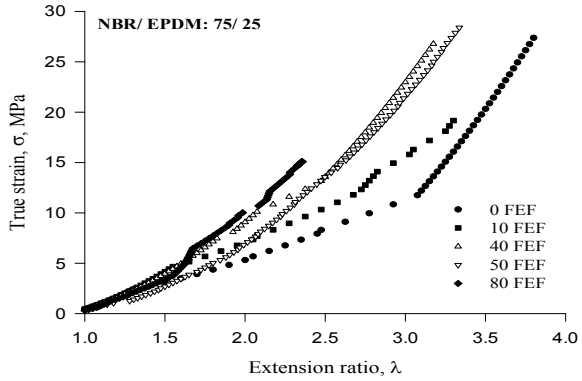

Fig. 2: Tensile stress- strain curves for NBR/ EPDM: 75/ 25 blend composites.

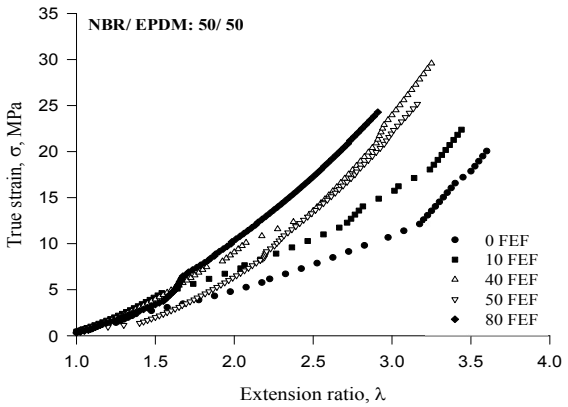

Fig. 3: Tensile stress- strain curves for NBR/ EPDM: 50/ 50 blend composites.

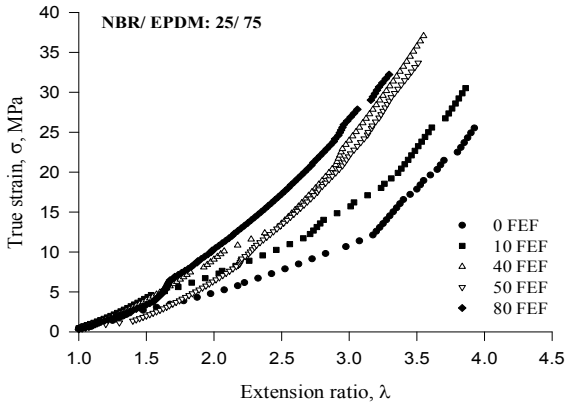

Fig. 4: Tensile stress- strain curves for NBR/ EPDM: 25/ 75 blend composites.

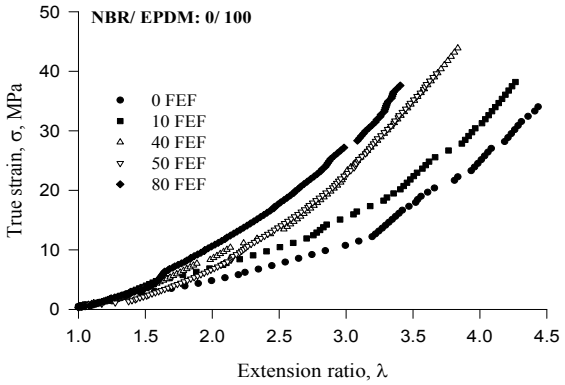

Fig. 5: Tensile stress- strain curves for FEF/ EPDM composites.

The variations in mechanical properties such as tensile strength and elongation at breaking point against filler loading for different blend composition are presented in Figures 6 and 7 respectively. It is clear that tensile strength of all blends increases with filler loading. However, the degree of reinforcement is found to be at its highest for pure EPDM rubber followed by 25/75 (NBR / EPDM) sample. The other

blend ratios showed relatively lower degree of reinforcement with FEF black. Both EPDM rubber and NBR are considered as non-self- reinforcing rubbers and FEF-black is regarded as being reinforcing filler [20]. Generally, non-self- reinforcing rubbers are reinforced through incorporation of reinforcing fillers.

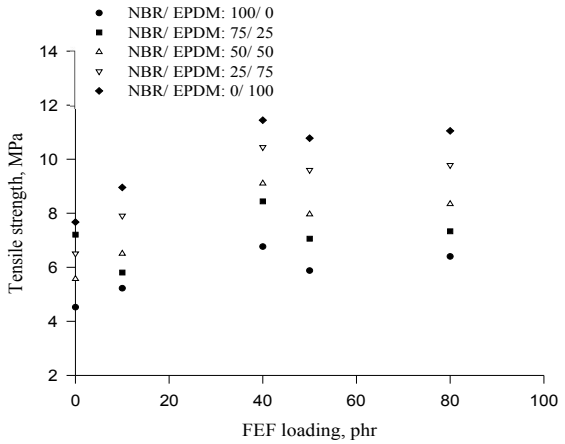

Fig. 6: The variation of tensile strength against filler loading for various blends.

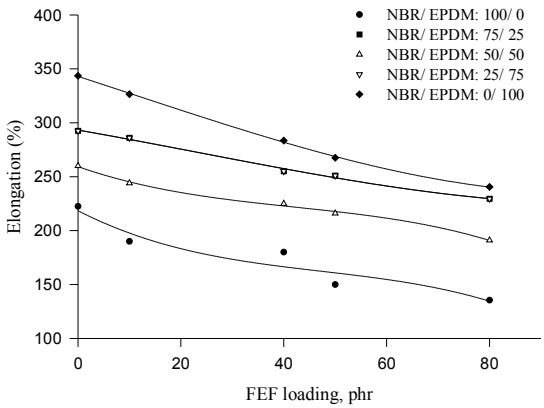

Fig. 7: Elongation at breaking point vs. filler loading for various blends.

The elongation at breaking point shows a decreasing behavior against filler loading for all systems. At very low filler loadings, when the matrix is not sufficiently reinforced, it can not sustain load and so failure occurs at lower elongations. By increasing filler loading, the molecular mobility decreases owing to the formation of physical bonds between filler particles and polymer chains (which is the basis for the mechanism of reinforcement). Consequently, the elongation at breaking point drops with increase in filler loading.

However, a higher elongation at breaking point is observed for EPDM and EPDM – rich blends, mainly because EPDM matrix has greater chain mobility than that of NBR matrix since the T_g of EPDM is -80^{0}C, whereas for NBR it is -40 ^{0}C [20].

3.2 Crosslinking density (η)

The crosslink density of an elastomer can be determined from swelling or mechanical measurements. The crosslinking density values of the homo polymers and blends have been calculated by using the following equation [21].

$$\eta = \frac{F}{2 A_0 \rho_p RT (\lambda - \frac{1}{\lambda^2})} \qquad (1)$$

Where F is the force required to stretch a specimen to an extension ratio (λ), A_0 the cross sectional area of the sample, R is the universal gas constant and T, the absolute temperature and ρ_p is the material density. The crosslinking density values are given in Table (3).

This high crosslinking density of 80 phr FEF loaded EPDM composite accounts for the superior properties of this composition. Meanwhile, one could observe that η increases with both CB content and EPDM concentrations.

Table (3): Crosslink density of NBR/ EPDM blend composites

Filler (phr)	Crosslinking density (η), mol/ kg			
	NBR/EPDM 0/ 100	NBR/EPDM 25/ 75	NBR/EPDM 50/ 50	NBR/EPDM 75/ 25
0	822	647	645	632
40	1285	1070	1106	764
80	1760	1340	1150	1066

3.3 Theoretical modeling

The mechanical properties of two-phase composites made up of a continuous polymer phase and particulate filler phase have been studied in great detail. The mechanical properties of particulate-filled composites are affected by a number of parameters such as filler orientation, filler/matrix adhesion and filler shape. In the literature, a number of theories and equations have been developed to predict the properties of the composites. The efficiency of load transfer from matrix to filler in a composite is strongly related to the optimum mechanical properties of the composite [22].

Following Johnson and Thomas [23] mechanical properties, we try to elucidate our results by modifying this treatment as follows. Theoretical treatment of the data of various composite models such as the parallel model, the series model, the Kerner model and the Kunori model were made use of to study the mechanical behavior of the blend. The parallel model (higher – upper – bound model) is given by the equation [24]

$$M = M_1 \phi_1 + M_2 \phi_2 \quad (2)$$

Where M is the mechanical property of the blend and M_1 and M_2 are the mechanical properties of the components 1 and 2, respectively and φ_1 and φ_2 are the volume fractions of the components 1 and 2 respectively. Here the components are considered to be arranged parallel to one another so that the applied stress elongates each of the components by the same amount.

In the lowest – lower –bound – series model, the components are arranged in series with the applied stress and are given by the equation [3]

$$\frac{1}{M} = \frac{\phi_1}{M_1} + \frac{\phi_1}{M_2} \quad (3)$$

Kunori et al [25] suggested a model when strong adhesive force exists between the blend components. In this model, the dispersed phase will contribute to the strength of the blend and the equation is:

$$\sigma_b = \sigma_m (1 - A_d) + \sigma_d A_d \quad (4)$$

Considering two possible fracture paths in a blend, Equation (4) can be modified as follows depending on whether the fracture is through the interface or through the matrix. When the fracture is through the interface:

$$\sigma_b = \sigma_m (1 - A_2^{2/3}) + \sigma_d \phi^{2/3} \quad (5)$$

when the fracture is through the matrix:

$$\sigma_b = \sigma_m (1 - \phi_d) + \sigma_d \phi_d \quad (6)$$

Where σ_b , σ_m and σ_d are the properties of the blend, matrix phase and dispersed phase respectively and φ_d is the volume fraction of the dispersed phase.

Figure (8) shows the theoretical and experimental curves of the tensile strength values of FEF/ EPDM composites. One may conclude that equation (5) (proposed by Kunori et al) gives a better fitting with the experimental data with respect to the other models.

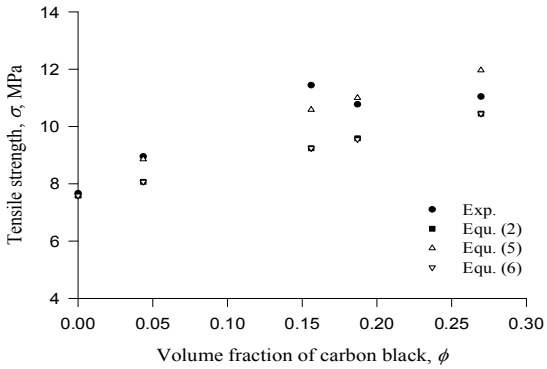

Fig. 8: Tensile strength vs. filler volume fraction fitted by difference models.

Conclusion

Results presented in this paper point to the existence of FEF carbon black loading, over which the properties of the NBR/ EPDM different blend ratio vulcanizates i.e., tensile strength and elongation at break are seen to pass through relatively sharp changes when plotted against the carbon black loading level. The presence of EPDM in the blend to accompanied by an enhancement in technological properties, which depends on the composition of both FEF and EPDM. The improvement in mechanical properties is supported by data on the increased content of crosslink density in these samples (obtained from stress – strain data measurements) upon FEF and EPDM loading. The degree of reinforcement achieved through incorporation of FEF – black is the highest for pure EPDM rubber followed by samples enriched with EPDM.

Kunori et al equation was found to give better fitting with the experimental results of the dependence of tensile strength on the FEF black loading.

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