Effect of Different Types of Carbon Black on the Mechanical and Acoustic Properties of Ethylene–Propylene–Diene Rubber

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ABSTRACT: The effects of the incorporation of different types of carbon black as fillers on some selected physical and mechanical properties of ethylene–propylene–diene rubber (EPDM) based compounds were studied with the results of density, ultrasonic wave velocity, and tensile measurements. Ultrasonic wave velocities (both longitudinal and shear) were measured at frequencies up to 4 MHz at room temperature. The density, ultrasonic attenuation coefficient, and tensile strength results showed that rubber mixes containing general-purpose furnace (GPF) black at a concentration of 25 phr had the best physical and mechanical properties. These results were interpreted to be due to the better compatibility of GPF black, which, because of its particle size and structure, filled the interstitial spaces in EPDM and provided better reinforcement of the elastomer. The use of a nondestructive technique such as ultrasonic measurement presents a new possibility for testing rubber and plastic products more efficiently. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1502–1508, 2010

Key words: compatibility; mechanical properties; rubber

INTRODUCTION

The use of fillers as reinforcements for rubber is almost as old as the use of rubber itself. The concept of reinforcement is related basically to composite materials built from two or more structural elements: the strength of one of these elements is imparted to the composite and combined with the other component. In these cases, strongly anisometric materials such as fibers or rods, with length/diameter ratios of many thousands, usually overlap one another over large sections and are bound together by the matrix, so their strength is transmitted from one region to another. A totally different mechanism must be responsible for the reinforcement imparted to the elastomer by particulate solids. These solids are not actually spherical in shape and are not so strongly anisometric that they can be said to overlap one another over a large portion of their length. Nor are they actually so strong that they would be expected to impart additional strength to a composite.[1]

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A wide variety of particulate fillers are used in the rubber industry for various purposes, of which the most important are reinforcement, material cost reduction, and processing improvements.[2,3] The reinforcement of elastomers is basically the enhancement of the strength and strength-related properties, abrasion resistance, hardness, and modulus.[4,5] In most applications, carbon black (CB) is used as the main reinforcing filler and increases the usefulness of rubber. When CB is compounded with rubber, all the mechanical properties are increased.[6,7]

For the rubber processing industry, relevant data for filled rubber compounds are, however, more important than those for the gum elastomer. The incorporation of CB as a reinforcing filler in rubber compounds meant for structural/engineering objects is a common practice. Such reinforcing filler incorporation commonly results in (1) an enhancement of the melt viscosity[8,9] with prominent development of a thixotropic character[10,11] and (2) a reduction of die swelling and extrudate distortion.[12] The incorporation of conducting CB particles as fillers along with selected curatives in an elastomer system may make the final vulcanizate somewhat electrically conducting and, at the same time, impart notable changes in its cure characteristics, including its scorch safety, cure and aging behavior, and mechanical and aging properties.[13]

In this article, we present a study using mechanical and acoustic test methods to illustrate the

TABLE I
Properties of the Different Types of CB

Type of CB	ASTM designation	Particle size (nm)
SAF	N110	20–25
ISAF	N220	24–33
HAF	N330	28–36
FEF	N550	39–55
GPF	N660	55–65
MT	N990	250–350
LB	—	90–130

efficiency of a certain type of CB in the reinforcement of ethylene–propylene–diene rubber (EPDM).

EXPERIMENTAL

Materials

EPDM was supplied by HK Chuangsheng Rubber & Plastic Co. (China). Different types of CB were purchased from Transport and Engineering Co. (Egypt). All other ingredients were laboratory-grade and were supplied by El Nasr Co. and Adwic (Egypt).

The different types of CB used in this study and their properties, as provided by the manufacturer, are listed in Table I, and their average particle sizes are illustrated in Figure 1.

Preparation of the rubber mixes

The rubber mixes were prepared on a two-roll mill (152 mm × 330 mm) at a friction ratio of 1 : 1.14 according to ASTM D 15-627. Curing was carried out at 153°C for the optimum curing time according to results estimated with an oscillating disc rheometer (MDR 2000; ASTM D 2084). The samples were vulcanized in a hydraulic press at 153°C and 14.71 MPa. EPDM mixes containing different types of CB and different amounts of general-purpose furnace (GPF) black are listed in Tables II and III, respectively.

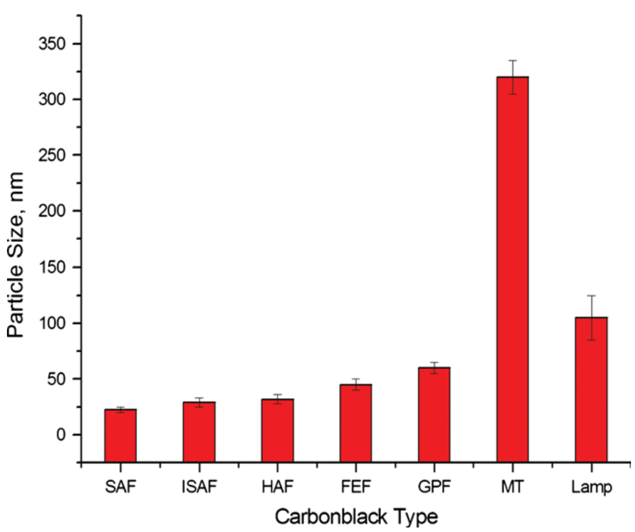

Figure 1 Particle sizes of the different types of CB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
EPDM Mixes Containing Different Types of CB

Ingredient	Mix code					
	C5	C6	C7	C8	C9	C10
EPDM	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
SAF black	25	—	—	—	—	—
HAF black	—	25	—	—	—	—
FEF black	—	—	25	—	—	—
MT black	—	—	—	25	—	—
ISAF black	—	—	—	—	25	—
LB	—	—	—	—	—	25
Processing oil	5	5	5	5	5	5
Antioxidant (6PPD)	1.5	1.5	1.5	1.5	1.5	1.5
Accelerator (MBT)	2	2	2	2	2	2
Sulfur	2	2	2	2	2	2

6PPD = *N*-(1,3-dimethylbutyl)-*N*-phenyl-*p*-phenylene diamine; MBT = mercaptobenzothiazole.

Mechanical testing

Mechanical testing was carried out with a Zwick (Germany) model Z010 tensile testing machine at 23 ± 2°C and at a crosshead speed of 500 mm/min with dumbbell-shaped tensile specimens according to ASTM D 412-80.

Density measurements

The density of all rubber samples was calculated via Archimedes' principle with toluene as follows:

$$\rho = \rho_b \left(\frac{W_a}{W_a - W_b} \right) \quad (1)$$

TABLE III
EPDM Mixes Containing Different Amounts of GPF Black

Ingredient	Mix code				
	C0	C1	C2	C3	C4
EPDM	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5
GPF black	0	25	50	75	100
Processing oil	5	5	5	5	5
Antioxidant (6PPD)	1.5	1.5	1.5	1.5	1.5
Accelerator (MBT)	2	2	2	2	2
Sulfur	2	2	2	2	2

6PPD = *N*-(1,3-dimethylbutyl)-*N*-phenyl-*p*-phenylene diamine; MBT = mercaptobenzothiazole.

where ρ is the density of the rubber sample; ρ_b is the density of the buoyant; and W_a and W_b are the sample weights in air and the buoyant, respectively. The experiment was repeated three times, and the error in the density measurements for all rubber samples was ±1 kg/m^3.

Ultrasonic velocity measurements

The ultrasonic wave velocities were obtained via the pulse–echo technique by the measurement of the time that elapsed between the initiation and receipt of the pulse appearing on the screen of a flaw detector (USM3, Kraütkramer) by a standard electronic circuit (54615 B, Hewlett–Packard). The velocity was, therefore, calculated by the division of the round-trip distance by the elapsed time according to the following relation:

$$U = \frac{2x}{\Delta t} \tag{2}$$

where U is the ultrasonic wave velocity, x is the sample thickness, and Δt is the time interval.

All velocity measurements in this study were carried out at the frequency of 2 MHz and at room temperature (25°C). The estimated error in the velocity measurements was ±1 m/s for the longitudinal wave velocity and ±2 m/s for the shear wave velocity.

The attenuation coefficient was then calculated with the following equation:

$$\alpha = \frac{20\ \log (l_1/l_2)}{2x} \tag{3}$$

where α is the attenuation coefficient and l_1 and l_2 are the heights of the two successive echoes displayed on the cathode ray oscilloscope. The estimated accuracy of ultrasonic attenuation was about ±0.3 dB/cm.

Determination of the elastic moduli

The elastic moduli (the shear modulus and Young's modulus), microhardness, and Poisson's ratio of EPDM samples filled with different types and/or amounts of CB were determined from the measured ultrasonic velocities and density with the following relations:[14]

$$\begin{aligned} L &= \rho U_l^2 \\ G &= \rho U_s^2 \\ E &= (1+\sigma)\,2G \\ \sigma &= \left(\frac{(L-2G)}{2(L-G)}\right) \\ H &= \frac{(1-2\sigma)E}{6(1+\sigma)} \end{aligned} \tag{4}$$

where L is the longitudinal modulus, U_l is the longitudinal wave velocity, U_s is the shear wave velocity, G is the shear modulus, E is Young's modulus, H is the microhardness, and σ is Poisson's ratio. The ultrasonic technique differentiated between Young's modulus, which is a function of the shear and longitudinal ultrasonic wave velocities, and the longitudinal modulus, which is a function of the longitudinal velocity only. This enabled us to differentiate between changes taking place parallel to the polymer chains and perpendicularly to the polymer chain in an oriented polymer sample.

RESULTS AND DISCUSSION

Effect of the type of CB on EPDM reinforcement

The mechanical properties of the EPDM mixes containing different types of CB are shown in Figure 2. For all seven types of CB used, GPF black showed the highest value of Young's modulus and superior tensile strength and elongation at break in comparison with the other types of CB. This only illustrates the better reinforcement of this particular mix with GPF black. This might be an indication that the size of GPF black is most suitable for filling the interstitial spaces in EPDM for better reinforcement. The actual mechanism of reinforcement with CB is not yet fully understood; however, different types of CB contain different types of functional groups on their surfaces, and this helps to increase the crosslink density and the molecular weight between two crosslinks and in turn improves the mechanical properties of particular mixes to different extents.[1] Also, the rate of drawing and other drawing conditions affect the behavior of the stress–strain curve. Here

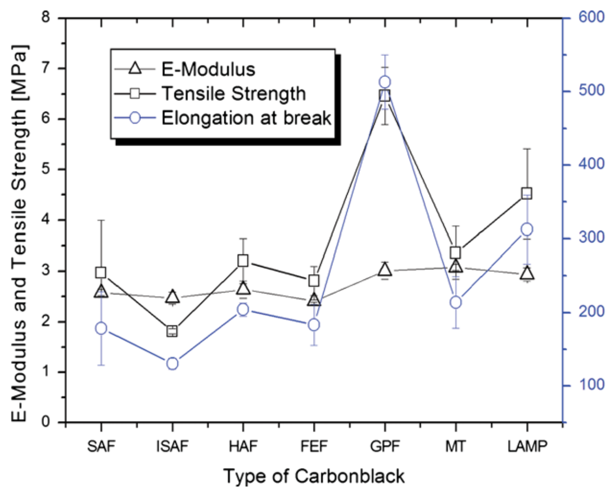

Figure 2 Variation of the mechanical properties of the EPDM mixes containing different types of CB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

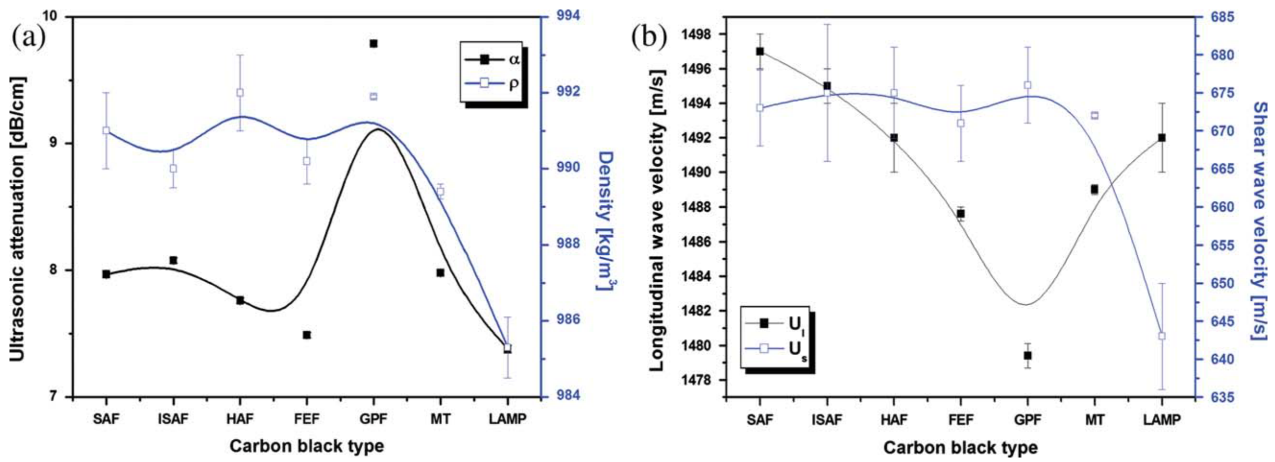

Figure 3 Variations of (a) the density (ρ) and ultrasonic attenuation (α) and (b) both ultrasonic wave velocities [longitudinal (U_l) and shear (U_s)] with different types of CB in the rubber mixes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

we abide with the conditions explained in ASTM D 412-80.

The densities of samples containing different types of CB were measured as explained previously. It is well known that the density of a solid material depends on many factors, such as the structure, coordination number, crosslink density, and dimensionality of interstitial spaces.[15] Experimental values of the density as a function of the CB type are shown in Figure 3(a). Higher density values were obtained for those EPDM mixes containing 25 phr high abrasion furnace (HAF) and GPF (992 and 991.9 kg/m^3, respectively).

Density exerts an economic impact on shipping and storage costs because with bulk grades these costs are, to an extent, based on volume. Lighter materials are associated with higher costs, and higher densities are therefore economically desirable. It is known that individual CB aggregates occur in what appear to be random constructions of randomly sized particles. Aggregates can occur as semispherical groupings of particles, or they can occur as groupings with a distinctly long dimension. Aggregates can have a very dense, solid construction or an open, lattice-like configuration. It can be suggested that HAF and GPF are adequately sized to fill the interstitial spaces in EPDM because of their preferable particle/aggregate size. Accordingly, aggregate interstitial spacing is reduced, and this affects the mobility of that portion of the elastomer bridging the space. Therefore, this might be the reason for the higher density values in the EPDM samples filled with HAF and GPF. In other words, the total volume of the bulk sample is kept constant, whereas the mass is increased because of the filling of the interstitial spaces with the denser HAF and/or GPF aggregates, which increase the overall density of the sample.

The ultrasonic attenuation coefficient, measured at a frequency of 2 MHz, changed with the type of CB used as a filler in EPDM. It is clear from Figure 3(a) that the sample filled with GPF had higher attenuation values. The relationship between the ultrasonic wave velocities (longitudinal and shear) and the CB types for the investigated samples is shown in Figure 3(b). The longitudinal wave velocities were lowest for the sample filled with GPF (1479.4 m/s), whereas the shear wave velocity was highest (676 m/s).

According to Higazy and Bridge,[16] the longitudinal strain changes directly with the bond stretching force constant. Therefore, in the investigated samples, the longitudinal strain in the main chains seemed to be unaffected by the filling of EPDM with GPF as the longitudinal ultrasonic wave velocity was equal to 1479.4 m/s versus 1477 m/s for EPDM without CB. On the other hand, as reported previously,[16] the shear strain changed with the bond bending force constant. Thus, the shear strain was affected by filling with GPF as the shear ultrasonic wave velocity showed the highest value of 673 m/s for the GPF-filled rubber sample in comparison with the EPDM mixes filled with other types of CB. All the values reported for the ultrasonic shear velocities were higher than those obtained for unfilled EPDM samples, as discussed later.

Figure 4(a) illustrates that Young's modulus was almost constant for the different CB types, with the exception of lamp black (LB), which showed inferior values. The values of the elastic properties for the EPDM samples filled with HAF and GPF were slightly higher: 1.241 and 1.240 GPa for Young's modulus and 0.452 and 0.453 GPa for the shear modulus, respectively.

Spherical aggregates loaded in a compound will inhibit the elasticity of the compound to a degree, but when these aggregates have a certain shape

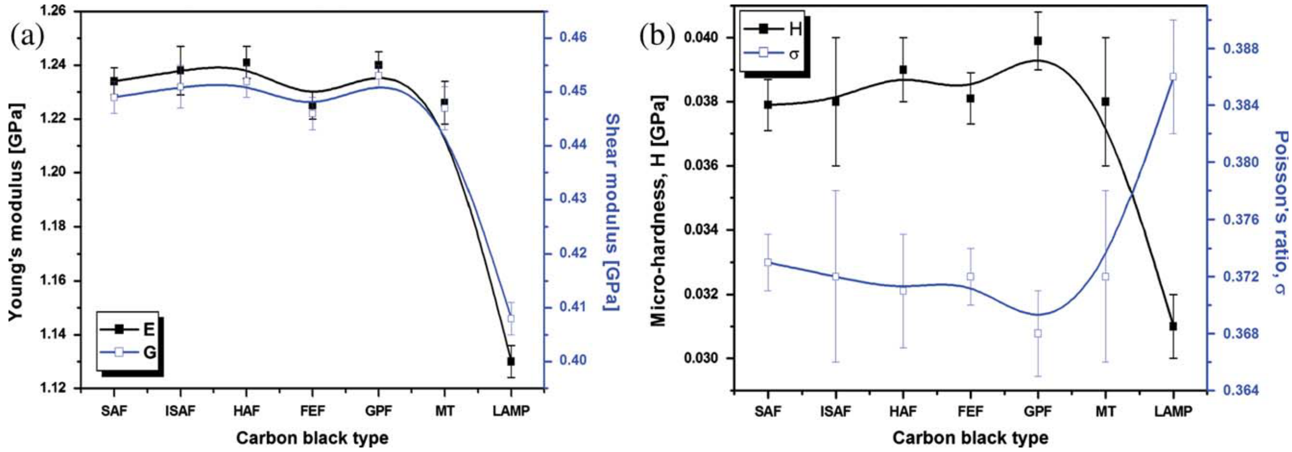

Figure 4 Plots of (a) Young's modulus (*E*) and the shear elastic modulus (*G*) and (b) the microhardness (*H*) and Poisson's ratio (σ) with different types of CB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

factor, that is, a long dimension, they will act as if they were very short fibers and interfere with the elastic mobility of the polymer in which they are dispersed.[1] This will lead to a stiffening effect that is more pronounced with the structure than with the particle size. Therefore, the higher elastic moduli for EPDM filled with HAF and GPF may have been due to the presence of these fillers as short fibers, which stiffened the rubber structure.

Figure 4(b) shows that the microhardness was higher for the rubber sample filled with GPF (0.0399 GPa) versus the HAF-filled rubber (0.039 GPa), and hence the observed increase in the microhardness was related to the increase in the rigidity of the GPF-filled EPDM. According to Rao,[17] Poisson's ratio depends on the dimensionality of the structure and crosslink density. The crosslink density was calculated according to Higazy and Bridge[16] with the following equation:

$$\sigma = 0.28(N_c)^{-0.25} \quad (5)$$

where N_c is the crosslink density.

Figure 4(b) shows a lower value of Poisson's ratio (0.368) and a higher value of the crosslink density (0.335) for the rubber sample filled with GPF.

The higher microhardness of the rubber filled with GPF confirmed the results for the elastic moduli. Also, the lower value of Poisson's ratio and higher value of the crosslink density for the rubber sample filled with GPF (CB) meant that GPF had the higher reinforcement potential. Therefore, the results for the density, ultrasonic attenuation, ultrasonic wave velocities, elastic moduli, microhardness, Poisson's ratio, and crosslink density have led us to conclude that the GPF filler acts as a crosslinker and tends to increase the crosslink density of EPDM and thus is better for the reinforcement of EPDM than super abrasion furnace (SAF) black, intermediate super abrasion furnace (ISAF) black, HAF black, fast extruding furnace (FEF) black, medium thermal (MT) black, and LB.

Effect of the concentration of CB on EPDM reinforcement

Another set of mixes was prepared with different concentrations of GPF black, as illustrated in Table III. Figure 5 shows that the mechanical properties improved gradually as the concentration of CB was increased from 0 to 100 phr. This effect can be explained in two ways. First, CB evened out the inner stresses in the rubber and allowed more molecular chains to effectively carry the load. The homogeneous stress distribution in turn caused a great improvement in the tensile strength. Second, CB had an effect not only on the elastomer but also on the bound condition between the elastomer and other

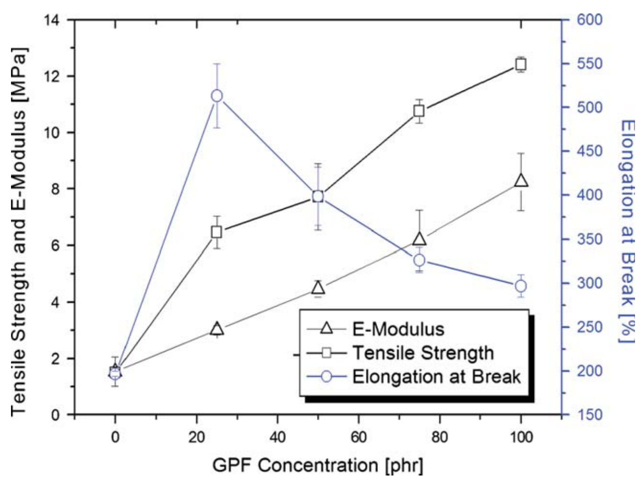

Figure 5 Variation of the mechanical properties of the EPDM mixes containing different loadings of GPF black. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

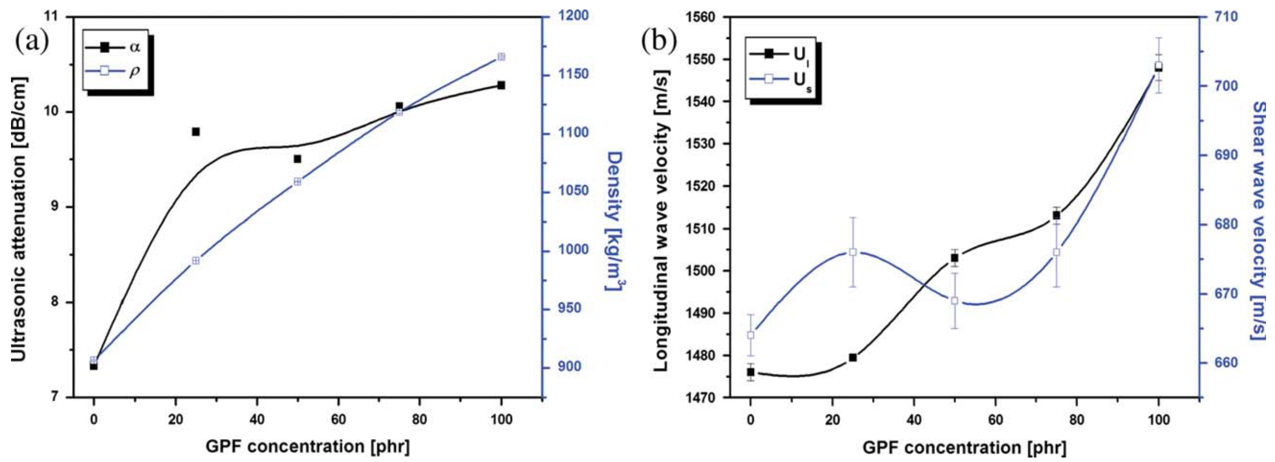

Figure 6 Variations of (a) the density (ρ) and ultrasonic attenuation (α) and (b) both ultrasonic wave velocities [longitudinal (U_l) and shear (U_s)] with different concentrations of GPF in the rubber mixes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

particles in the rubber mix. In the absence of CB, the inner voids led to stress concentration within the sample, and this resulted in rupture at a low stress. Therefore, the tensile strength remarkably increased with the addition of CB.[18] However, mixes containing 25 phr GPF black showed the highest elongation at break values, and this might have been due to the mobility of the polymer chains being highest at this particular concentration. This also indicated that using 25 phr GPF was most efficient in reinforcing EPDM because it imparted good tensile properties and the highest elongation at break values.

Figure 6(a) presents the increase in the density of EPDM with an increase in the concentration of the GPF filler from 0 to 100 phr. This increase in the density was due to the increase in the filler aggregation and the increased density of CB in comparison with that of EPDM. It is also clear from the figure that the ultrasonic attenuation of EPDM increased with the GPF concentration increasing from 0 to 100 phr at the frequency of 2 MHz. Moreover, the presence of a maximum in the ultrasonic attenuation with 25 phr GPF, which was higher than that with 50 phr GPF, indicates that the crosslink density increased with increased GPF aggregation.

Figure 6(b) presents plots of the ultrasonic wave velocities with the GPF concentration. The increases in both ultrasonic wave velocities (longitudinal and shear) were due to the increase in the filler aggregation, which caused a reduction of the interstitial spacing.[1] Moreover, the presence of maxima in the shear ultrasonic wave velocity with 25 phr GPF confirmed the trend of ultrasonic attenuation with the GPF concentration in Figure 6(a), and this means that the shear strain was more highly affected with 25 phr GPF filling than 50 phr GPF filling.

Figure 7(a) shows the variation of both Young's modulus and the shear elastic modulus with the

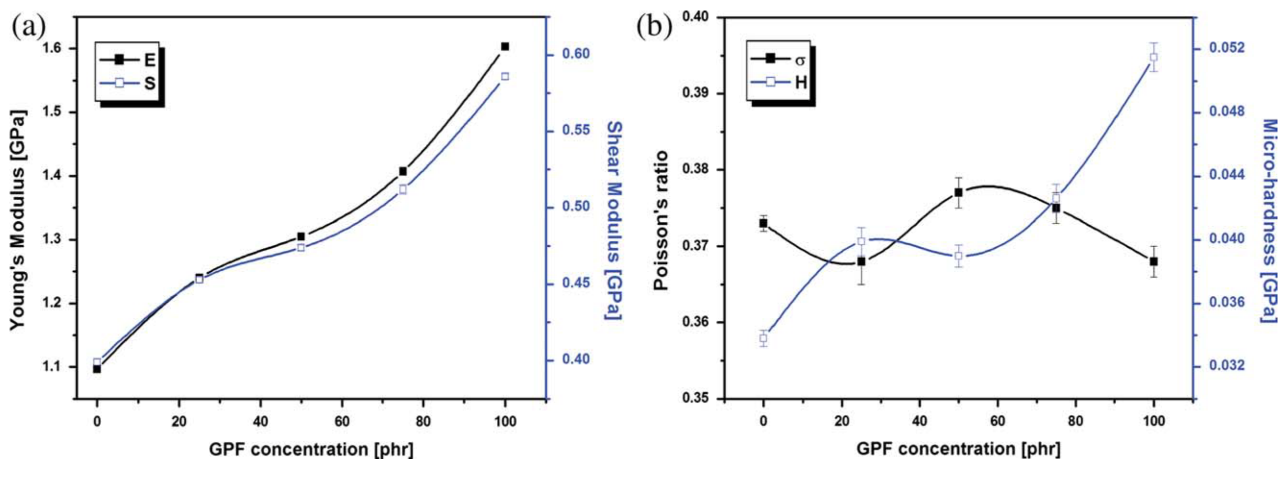

Figure 7 Plots of (a) Young's modulus (E) and the shear elastic modulus (S) and (b) the microhardness (H) and Poisson's ratio (σ) with different concentrations of GPF in the rubber mixes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

GPF concentration. The increase in Young's modulus and the shear elastic modulus from 1.097 and 0.399 GPa to 1.603 and 0.586 GPa, respectively, can be explained by the reinforcing effect of the filler on the polymer material:[19] the GPF particles had clustering trends leading to filler networking. The CB filler induced structural modifications of the elastomer chain segments mostly through physical interactions, including occlusion within the pores of the filler particles, and partly through chemical anchorage of the elastomer chain molecules or segments thereof on the surface of the CB filler particles; the traces of functional groups (OH, C=O, COOH, etc.) present in them may also explain the observed effects.

The increase in the values of the microhardness with the GPF concentration (from 0.0338 to 0.0515 GPa), as shown in Figure 7(b), confirmed the increased stiffening of EPDM with the GPF concentration. Furthermore, the higher value of the microhardness with 25 phr GPF versus 50 phr GPF confirmed the increased crosslink density with 25 phr GPF.

Poisson's ratio showed interesting results with the GPF concentration increasing up to 100 phr, as illustrated in Figure 7(b). Its values decreased from 0.373 for the zero-filled sample to 0.368 for the 25 phr GPF concentration; after that, there was an increase to 0.377 with the 50 phr concentration, which was followed by a decrease to 0.370 with the GPF concentration increasing up to 100 phr. These results indicated that the EPDM sample filled with 25 phr GPF had a higher crosslink density of 0.335, as calculated with eq. (5). These results can lead to the conclusion that the GPF concentration of 25 phr is the best filling concentration for EPDM.

CONCLUSIONS

GPF black acted as the best reinforcement CB filler for EPDM. The results for the mechanical, physical, and acoustic properties showed that mixes containing 25 phr GPF had better reinforcement characteristics than those containing other types and/or concentrations of CB. The ultrasonic measurements used to assess the degree of reinforcement of EPDM by CB were clearly in accordance with the more widely used mechanical and physical measurements. However, the combination of both techniques provides more insight into microscopic changes that eventually lead to changes in the macroscopic properties of the final rubber mix. The use of the ultrasonic technique also provides the possibility of using a nondestructive test to evaluate and characterize rubber mixes for different applications. It is obvious that elastic properties obtained from mechanical testing and ultrasonic measurements show the same behavior, but they do not necessarily have the same values.[20,21] The high shape factor of GPF in EPDM makes it act like short fibers and interfere with the elastic mobility, and this leads to the reinforcement of the rubber mix.

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