# EFFECT OF CARBON BLACK FILLERS ON HIGH STRAIN RATE PROPERTIES OF NATURAL RUBBER

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# EFFECT OF CARBON BLACK FILLERS ON HIGH STRAIN RATE PROPERTIES OF NATURAL RUBBER

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# ABSTRACT

The objective of this research is to examine the effect of carbon black fillers on the high strain rate properties of natural rubber. Tensile tests were conducted on unfilled and carbon black filled natural rubber with 25, 50, and 75 phr of N550 carbon black, using an INSTRON universal material testing machine and Charpy impact apparatus. Complete Cauchy stress-extension ratio curves at constant strain rates as well as tensile strength and extension at break were obtained for strain rates ranging from 0.1 s<sup>-1</sup> to 588 s<sup>-1</sup>. Results showed that the unfilled and 25 phr carbon black-filled natural rubber were stiffer at strains greater than 300 % under quasi-static loading than they were under high rates of loading. This was due to insufficient time for strain-induced crystallization to occur in these materials at high strain rates. At quasi-static rates of loading, carbon black filler increased the tensile strength of natural rubber with a maximum increase at 25 phr carbon black. The tensile strength decreased with carbon black above this amount. Small amounts of carbon black enhanced strain-induced crystallization, whereas too much carbon black impeded strain-induced crystallization, which is the main strengthening mechanism in NR under quasi-static loading. The tensile strength increased progressively with higher amounts of carbon black at high rates of loading. Carbon black increased the tensile strength of natural rubber at high strain rates because the rubber had not strain crystallized and was still in an amorphous state.

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# CHAPTER I

#### INTRODUCTION

The strain rates in tires can be well above those obtained from conventional quasi-static tests, which are generally below  $1 \text{ s}^{-1}$ . Consider a standard 205/60R15 pneumatic tire. This tire has a section width of 205mm, an aspect ratio of 60 and a rim diameter of 15in. Assume that when it is mounted on a vehicle traveling at a speed of V mph, the tire has a footprint, as shown in Fig. 1, of roughly 8in due to the weight of the vehicle. As the tire rolls, rubber treads in the footprint of the tire are loaded and unloaded per tire revolution. Since 8in has to be in contact with the ground during every revolution of the tire, the total loading/unloading time in one revolution was calculated to be

 $\frac{8in * 3600(sec/hour)}{63360(in/miles) * V(mph)}$ . Table 1 shows the total loading and unloading time for

different car speeds. The faster the vehicle travels, the shorter is the loading/unloading time of the tread in the footprint. Assume that the loading time is twice as long as the unloading time [1] and consider rubber undergoing a strain of 100%. A local strain of this value is not unreasonable for a tread in the footprint area. Take for example a vehicle traveling at the speed of 65 mph. Then the strain rate involved in stretching the rubber to 100% is 214 s<sup>-1</sup> (=3/(2\*0.007 s)).



Figure 1.1. Footprint of a tire.

Table 1.1. Estimated loading/unloading time in footprint and strain rate to reach 100% in standard 205/60R15 tire (calculations based on loading time being twice as large as unloading time).

Vehicle Speed (mph)	Loading/Unloading time in footprint (ms)	Strain Rate (s <sup>-1</sup> ) for strain of 100 %
35	13	115
55	8.3	180
65	7.0	214
75	6.1	245
85	5.3	283
95	4.8	312
125	3.6	416

The faster the vehicle travels, the higher this strain rate would become. The third column in Table 1 shows calculated strain rates for a 100% strain at the various vehicle velocities. For an automobile traveling between 35-125 mph, the strain rates vary from 155-416 s<sup>-1</sup>. These rates are clearly not quasi-static and can be even higher if one considers the tread at breaking strains, several times greater than 100% strain. The above analysis serves as a motivation for the development of constitutive models to predict rubber material response at high strain rates. This thesis is concerned with the acquisition of high strain rate material properties, which will become essential material as input data for high strain rate constitutive models for unfilled and filled natural rubber. The study will illustrate the differences in the deformation and fracture behavior of natural rubber (NR) under high strain rates and what is observed under quasi-static loading. Quasi-static tests will be conducted on an INSTRON electro-mechanical machine to obtain the quasistatic properties, while high-speed tensile tests will be conducted using a Charpy tensile impact apparatus developed by Bekar et al [2]. The tensile impact machine is capable of achieving very large strains, in excess of 100 % and strain rates up to  $1,000 \text{ s}^{-1}$ .

Dynamic material properties of elastomers can be specified in the time domain or the frequency domain. Time domain material properties describe transient material response and are used for rubber components under monotonic loading such as shock and impact. Frequency domain material properties describe vibration or cyclic material response and are used for rubber components under cyclic loading such as a rolling tire or engine mount. Material properties in the frequency domain are restricted to linear viscoelastic systems. In such systems it is assumed that stress is directly proportional to strain and strain rate. Dynamic materials such as the storage and loss modulus are used to describe the behavior of rubber in terms of a linear spring and a linear viscous dashpot model. Hence these properties hold good only in small strain regions where the stress is nearly linear with strain and strain rate. When in tension, elastomers are not only nonlinear but also hyperelastic. They can reach extensions as high as 300-500% before breaking. Concepts such as storage and loss modulus loose their meaning since the rubber can neither be modeled as a linear spring nor a linear viscous dashpot. Conventional dynamic mechanical tests used to obtain material properties in frequency domain should not be used to determine the large strain nonlinear viscoelastic characteristics of the material. Moreover fracture properties of the rubber cannot be determined from DMA tests on rubber. Deformation and fracture properties of NR under transient loads will be measured in this study. Dynamic stress-extension ratio curves at high strain rates will be determined up to the tensile strength of the material. Such material properties can be used for failure analysis of rubber components under dynamic loads, such as the tearing of rubber in a tire tread, or tire wear.

Most tires are made of either NR or Styrene Butadiene Rubber (SBR). Unlike other rubbers, NR has the unique ability to undergo strain-induced crystallization. The cis-1,4-polyisoprene structure of NR contains macromolecules that are configured identically and spontaneously pack together as crystallites either at low temperature (the maximum packing rate occurs at about -25 °C) or at room temperature upon stretching [3]. Strain-induced crystallization leads to important mechanical properties such as green strength, tear strength and gum tensile strength. Synthetic rubbers like SBR, on the other hand, cannot crystallize and are about 90% weaker when compared to NR. Carbon black is often used as a filler material to improve the strength of SBR. It can increase the strength of SBR more than tenfold. It has been mentioned in Ref. [4] that carbon black has very little effect on the tensile strength of NR since most of the strength of NR is due to strain-induced crystallization. Carbon black, however, will improve the tearing strength and abrasion resistance of NR.

Since all tires are made of rubber reinforced with carbon black and/or silica, it is important to understand the role of carbon black fillers on the deformation and fracture of NR at high strain rates. Natural rubber, unfilled and filled with 25, 50 and 75 phr of N550 carbon black, will be used to examine the effect of carbon black on the high strain rate properties of NR. High-speed tensile tests will be conducted on rubber specimens to obtain stress-extension ratio curves at strain rates in the range 10-10<sup>-3</sup> s<sup>-1</sup>, using a tensile impact apparatus developed earlier by Bekar et al. [2]. Chapter II discusses high speed testing of rubber and reviews previous high strain rate data on SBR using this tensile impact apparatus. Specific properties of natural rubber and their fillers will be explained in Chapter III. Details of the Charpy tensile impact apparatus, the experimental setup and specimen preparation for the unfilled and filled NR will be presented in Chapter IV. This will be followed by experimental results and discussions in Chapters V and VI. Finally, conclusions and recommendations for future work will be given in Chapter VII.

# CHAPTER II

#### DYNAMIC TESTING OF RUBBER

Elastomers, in particular rubbers, are used in a wide variety of products ranging from rubber hoses, isolation bearings, shock absorbers to tires. Owing to mechanical properties such as low modulus and large extensibility (strains greater than 100% before break), they have been used over the centuries to alleviate the damage caused by shock and impact loads [5]. A great deal of dynamic testing and modeling of polymeric materials has been done in the frequency domain, where the sample is vibrated under very small strain amplitude and over a wide range of temperatures. The strain amplitude is usually kept small so that heat does not develop within the material during the test. These tests, known as Dynamic Mechanical Analysis (DMA) tests [6], are based on linear viscoelastic material response and strains must be confined to a few percent. Dynamic Material Analysis tests are not appropriate to determine the large strain, nonlinear viscoelastic characteristics of elastomers. In the linear viscoelastic region, timetemperature superposition may be used to extrapolate data at higher frequencies by Most researchers employ the time-temperature lowering the temperature [7]. superposition, i.e., Williams-Landel-Ferry (WLF) equations [8] to analyze the high strain rate behavior, but the data generated by time-temperature shift may not reliable when rubber experiences very high rates [9].

Due to the difficulties in combined high strain rate and large deformation testing, high rate tensile data for large strains and high strain rate are not commonly found in literature. Results of high speed testing were reported as early as 1934 by Nadai and Manjoine [10] and in 1948 by Villars [11], in which energy from a huge moving flywheel was used to stretch the test specimen held in a movable grip. Villars [11] reported some results for the tensile strength and breaking extension of dumbbell specimens of several gum and filled vulcanizates extended at strain rates between 100-100 s<sup>-1</sup>. In 1952, Dogadkin and Sandramirskii [12] published data on GR-S gum vulcanizates in the strain rate region of 0.0002-0.2 s<sup>-1</sup>. In 1960, Greensmith [13] published load extension data using ring specimens extended at various rate from 10<sup>-3</sup>-10 s<sup>-1</sup>. In 1962 Dannis [14] reported strength and elongation values of rubber by dropping weights down a chimney onto an instrumented specimen carriage. Kainradl and Handler [15] used dumbbell specimens to obtain strength measurements of filled vulcanizates in the strain rate regions of 10<sup>-2</sup>-10<sup>3</sup> s<sup>-1</sup>. All the above-mentioned studies do not give complete load-extension curves until the specimen breaks.

Material tests for high strain rate and large strain applications have only been developed in recent years due to technological advances in measurement devices and high speed data acquisition. Researchers have used the Split Hopkinson Pressure Bar (SHPB) apparatus [16-22], to obtain high strain rate properties of rubbers mostly in compression. This apparatus was developed primarily for studying high strain rate behavior of metals and not elastomers. The metal bars in the traditional SHPB are usually replaced with polymeric bars so that appreciable strains can be detected in the strain gages. Another method of obtaining tensile stress-strain curves for rubber at high rates is the expanding ring technique [23]. In the expanding ring technique, the material is placed around a cylinder which rapidly expands due to an explosion within the cylinder. The material expands circumferentially at high strain rates, while receiving a compressive preload in the radial direction. Since the stress history affects the subsequent stress-strain behavior of a viscoelastic material, data from expanding ring tests does not always agree with results from other tests. In fact, high strain rate material data among different material testing laboratories are usually never consistent or repeatable.

Bekar et al. [2,24,25] developed a simple tensile impact apparatus to measure deformation and fracture properties of unfilled Styrene Butadiene Rubber (SBR) under high strain rates. In these experiments, it was found that the modulus of SBR increased with increasing strain rate up to  $325 \text{ s}^{-1}$ . Beyond  $325 \text{ s}^{-1}$ , the modulus did not change with increasing strain rate. The stress-extension ratio curve at this critical point was termed a "locking" curve. It was proposed that the increase in modulus at high rates of loading resulted from the lack of relaxation time in the chain molecules. Three deformation and fracture regimes were identified for unfilled SBR as shown in Fig. 2.1. Regime 1 occurred from quasi-static rates to about 190 s<sup>-1</sup>. In Regime 1, the tensile strength and fracture strain increased with increasing strain rate. Regime 2 occurred between 190- $325 \text{ s}^{-1}$ , and in this regime, the tensile strength increased but the fracture strain decreased with increasing strain rate. In Regime 3, which occurred above  $325 \text{ s}^{-1}$ , both the tensile strength and fracture strain decreased with increasing strain rate. A similar study on

carbon black-filled natural rubber (NR) will be performed in this thesis. Natural rubber is a more complicated elastomer than SBR and the role of carbon black on high strain rate properties of rubber has never been addressed before. The following chapter provides the reader with a review of NR and carbon black fillers.



Figure 2.1. Deformation and fracture regimes of unfilled SBR [2].

# CHAPTER III

### NATURAL RUBBER

## 3.1 Natural Rubber

The structure of NR is thought to be completely cis-1, 4-polyisoprene as shown in Fig. 3.1, except for the chain ends [3]. This polymer contains a high degree of long-chain branching [26, 27] which is associated with the presence of small numbers of non-hydrocarbon groups distributed along the chains [27]. Because the macromolecules of NR are configured identically (stereoregular), they tend to spontaneously pack together as crystallites upon straining. This phenomenon known as strain-induced crystallization, imparts outstanding green strength to NR.



Figure 3.1. Molecular structure of cis-1,4 -polyisoprene.

During strain-induced crystallization the molecular chains tend to align in the direction of stretch forming a filamentous structure. The filamentous structure formed as a result of crystallization prevents cracks from growing until catastrophic rupture occurs.

This leads to high tensile strength of crystallizable rubbers. Due to the lack of strain induced crystallization in amorphous rubbers, they tend to be weaker than the crystallizable rubbers. The tensile strength of unfilled NR is about 21 MPa (3.04 ksi), which is greater than that of unfilled SBR which is about 2.1 MPa (0.3 ksi) [28]. The incorporation of reinforcing carbon black raises the strength of amorphous rubbers to a level equivalent to that of crystallizable rubber. Contrary to this the crystallites, in NR, developed during extension of unfilled rubber increase tensile strength to such an extent that addition of carbon blacks does not increase it much further. Prolonged exposure of NR to sub-zero temperatures and high strains causes crystallization decreases with increase in temperature [32]. Hence the degree of crystallinity of NR depends both on strain and temperature.

# 3.2 Fillers

Fillers can increase the strength of amorphous rubber more than 10 fold. The choice and loading of filler depends primarily on the product and the vulcanizate properties required. Fillers are added to impart strength, stiffness, abrasion and resistance [33]. Among the different types of fillers available, carbon black fillers are the most widely used. Carbon black fillers consist of about 90-99% elemental carbon with oxygen and hydrogen as other main constituents. They are obtained by the partial combustion or thermal decomposition of hydrocarbons and are widely used as reinforcing fillers in elastomers, plastics and paints [34, 35]. Carbon black fillers can be divided into three categories [36]:

- (1) Small particle size abrasion furnace blacks (N100-N300 series), which give vulcanizates the highest strength properties and highest changes in stiffness with strain amplitude.
- (2) Semi-reinforcing furnace blacks (N500-N700 series), which give slightly lower strength properties and smaller changes in stiffness with strain amplitude.
- (3) Diluent thermal blacks (N880-N990), which give much lower strength properties and smaller changes in stiffness with strain amplitude.

The 100, 200 and 300 series are used in tire tread, while the 500 and 600 series are used for the tire carcass. The N550 carbon black chosen for this study is not only used to make tires but also automotive belts, seals, weather strip, O-rings and gaskets, engine mounts, anti-vibration dampeners and wiper blades. The main characteristics of carbon black that influence the properties of carbon black-filled elastomers are particle size, aggregate size and surface area. The term 'aggregate' describes the chaining and clustering of carbon black particles [37]. It is defined as a discrete rigid colloidal entity that is the smallest dispersible unit, composed of extensively coalesced particles [38]. The most accurate means of measuring the particle size, surface area and aggregate size of carbon black is through an electron microscope. Table 3.1 gives the typical particle size, aggregate size and surface area values for carbon blacks [39]. It can be observed from Table 3.1 that as the particle size of the carbon black increases, the surface area decreases and aggregate particle size increases. Aggregate size, unlike other carbon black parameters, is affected by mechanical handling. For instance, high shear mixing, during preparation of the compound can cause significant aggregate breakdown.

ASTM number of	Mean <sup>a</sup> particle	EMSA <sup>a</sup> $(m^2/g)$	Aggregate size
Carbon Black	diameter (nm)		
N110	18	138	85
N220	21	121	-
N330	30	80	133
N550	56	41	240
N660	67	35	283
N990	285	9	436

Table 3.1. Typical particle size, surface area and aggregate size values for rubber grade Carbon Blacks.

<sup>a</sup> ASTM D 3849 Test Method for Carbon Black—Morphological Characterization of Carbon Black Using Electron Microscopy.

EMSA – Electron Microscope Surface Area.

In order to cause significant reinforcement, filler must possess high specific surface area and small particle size (less than 1  $\mu$ m). Small particles have large surface area to interact with the rubber and close particle-to-particle spacing in the compound. Another important characteristic of the filler is the structure. Large structured filler aggregate has a huge void volume in which the rubber molecules get trapped (occluded) during shear mixing [3]. A typical structure of carbon black agglomerate is shown in Figure 3.2. The combination of filler and bound rubber now acts as the reinforcing entity. Due to the self-reinforcing mechanism of NR, i.e., strain-induced crystallization addition of fillers does not significantly increase the tensile strength. However, it does improve resistance to tearing and abrasion.

# 3.3 Properties of filled vulcanizates

In rubber technology, it is customary to refer to the stress at a specified strain as "modulus". Smallwood [40] and Guth [41] found that the modulus (stiffness) of carbon

black-filled rubber is considerably higher than that of 'pure gum' under static or dynamic conditions, whether measured in shear, compression or extension. The addition of carbon black is known to improve the fracture properties of rubber materials [39].



Figure 3.2 Structure of carbon black agglomerate.

Carbon black enhances strain-induced crystallization for crystallizable elastomers such as NR [42, 43]. This was confirmed by X-ray study [44, 45] and differential scanning calorimetry. The tensile strength of rubber increases with increasing filler content up to a certain level. Beyond this level, the tensile strength decreases with higher filler concentrations. Goldberg et al. [46] suggested that this is because high amounts of carbon black fillers cause the carbon black to agglomerate into large clusters and these clusters impart flaws that can easily create cracks and lead to a catastrophic failure. The concentration at which maximum tensile strength is obtained, varies with the type of carbon black. For carbon black fillers with smaller particle size the maximum tensile strength is attained at lower concentrations than those for large particle sized carbon black fillers.

## CHAPTER IV

#### **TENSILE IMPACT EXPERIMENTS**

# 4.1 Materials

Samples of Natural Rubber (NR) with compositions listed in Tables 4.1 and 4.2 were prepared according to standard ISO 2393 methods [47]. The Institute of Polymer Science of The University of Akron provided the raw material and the specimens were made under the supervision of Mr. Robert Seiple. The various components were first weighed as specified in the Tables 4.1 and 4.2. The NR was then put into a shredder where it was shredded. Carbon black N550 was added at various amounts (25, 50 and 75 phr) and mixed in with the shredded NR. In the next step of preparation, the antioxidants (6PPD), accelerators (TMTD), antiozonants (MBTS), reinforcing agents and pigments (Zinc oxide), and softening agents (stearic acid) were added to the NR and carbon black mixture and mixed thoroughly into a homogenous mixture in a banbury. For the carbon black to be well dispersed in the rubber, the viscosity of the rubber must not be too low. If the viscosity of the rubber is too low, then the shear stresses will be insufficient to break the filler agglomerates into aggregates and thoroughly disperse them in the rubber.

Hence oil was added toward the end of the mixing cycle. The final stage involves curing of this mixture. Curing times, temperatures and pressures were determined from an Oscillating Disk type Rheometer (ODR) and are listed in Tables 4.1 and 4.2.

Ingredients	Amount (phr*)
NR	100
Process Oil	2
Stearic Acid	2
Zinc Oxide	5
6 PPD	1
Sulphur	2.75
MBTS	1
TMTD	0.1

Table 4.1. Composition of Unfilled NR.

Cure for 20 minutes at 300° F (150° C).

\* phr – parts by weight per 100 parts by weight of rubber.

Ingredients	Amount (phr*)
NR	100
Process Oil	5
Stearic Acid	2
Zinc Oxide	5
Carbon Black N 550	25,50,75
6 PPD	1.5
Sulphur	2.75
MBTS	1
TMTD	0.1

Table 4.2. Composition of Carbon Black filled NR.

Cure for 20 minutes at  $300^{\circ}$  F (150° C).

\* phr – parts by weight per 100 parts by weight of rubber.

The ODR described precisely and quickly curing and processing characteristics of vulcanizable rubber compounds. A test piece of the rubber compound was contained in a sealed test cavity under positive pressure and maintained at a specified elevated

temperature. A rotor was embedded in the test piece and was oscillated through small specified rotary amplitude. This action exerted a shear strain on the test piece and the torque (force) required to oscillate the disc depended upon stiffness (shear modulus) of the rubber compound. The stiffness of the specimen compound increased when cross links were formed during cure. The direct proportionality between the shear modulus and the cross linking density was based on the statistical theory of rubber elasticity. A plot of this torque value against time gives a typical graph called, 'The Cure Curve' or 'The Rheograph'. The Cure Curve obtained with rheometer is a fingerprint of the compound's vulcanization and processing character. The cure curve for the unfilled and the filled specimens is shown in Appendix A. The abscissa of the graph gives the time in minutes and the ordinate gives the torque in inch pounds. The peak of each curve represents the time at which the rubber specimen runs out of sulphur. They occur at about 20, 18, 16 and 14 minutes for the unfilled and 25, 50 and 75 phr carbon black filled NR specimens, respectively. These peaks, which later stabilize into plateaus, represent the maximum elasticity of the specimen.

As observed in the curve, the curing time of NR decreases as the amount of carbon black in the natural rubber increases. The reason behind this trend is the acidic nature of NR, the antioxidants, and the accelerators that were added to it. With the addition of alkaline carbon black, the overall medium of rubber changes to alkaline. This basic medium was a lot more favorable to cross-linking than the original acidic medium of NR and hence greater curing rates, i.e., lower curing times were observed. As the curing times of various unfilled and filled specimens were close to each other, we chose to cure all the specimens at 20 minutes. Doing so does not lead to any significant change

in the vulcanizate properties. Once the curing times and temperatures were determined, the rubber samples were placed in a hydraulic press and stamped for 20 minutes at a temperature of 300° F and a pressure of 300 psi. The size of the die was chosen such that the stamped samples were 152.4mm x 152.5mm x 2.54mm thick (6in X 6in X 0.1in thick). ASTM D412 [48] dumbbell and strip specimens were used for the quasi-static and dynamic tests, respectively. The gage dimensions were 25.4mm x 6.35mm x 2.54mm thick (1in x 0.25in x 0.1in thick). The dumbbell specimens were cut from a die and press, while the strip specimens were cut using a razor and hammer. An additional 25.4mm (1in) on either side of the 25.4mm (1in) gage length was allowed to grip the strip specimen as shown in Fig. 4.1. In Fig. 4.1, the bold lines show the actual tensile specimen dimensions, while the dash lines show the actual strip dimension that was cut.



Figure 4.1. Geometry of ASTM 412 strip specimen.

It is standard practice not to test rubber within 16 hours of vulcanization [49]. Cross-linking does not stop exactly when the rubber is taken out from the mold. It continues as the rubber cools to room temperature and even proceeds slowly at room temperature. Thus all material tests were conducted about one week after curing. The maximum time between vulcanization and testing is usually about 60 days [50]. To extend the testing period, the rate of cross-linking was slowed down by storing the specimens in a refrigerator at a reduced temperature of about  $40^{\circ}$  F.

# 4.2 Experimental Setup

The tensile impact experiment that was used to obtain the deformation and fracture characteristics of natural rubber under tensile impact loading was developed by Bekar et al. [2] and is shown in Fig.4.2. This tensile impact apparatus was used to obtain dynamic stress-strain curves of the ASTM D412 strip specimens. As shown in Fig. 4.2(a), the experiment uses a Charpy impact pendulum (maximum available energy of 300 ft lb) to impact a specially designed slider bar connected to two copper cables. The copper cables were directed around pulleys and attached to sliding guided bases with grips that hold opposite ends of the specimen. The guided bases were allowed to slide freely along steel rails via linear bearings.

The piezoelectric force sensors (PCB load cells) mounted on each guided base recorded the impact tensile force as the copper cables pulled on the guided base. The tensile force was actually measured as a compressive force on the backside of rectangular slots. The extension of the specimen was recorded by two RDP D5 Linear Variable Differential Transformers (LVDTs), which have a range of  $\pm 150$  mm and are also mounted on each of the guided bases. Figure 4.3 depicts the installation of dynamic load cells and LVDT on movable guided moving bases. An 8-Channel PCB 482A22 Signal Conditioner was used with the force sensors, and two RDP S7AC Transducer Amplifiers were used with the LVDTs. The data acquisition device used in the experiment was DATAQ DI-720-USB. It has the ability to collect 250,000 data per second. Since there

were two load cells and two displacement transducers or four channels, each channel could obtain up to 62,500 data points per second, which was deemed sufficient for this type of application.



Figure 4.2. Schematic diagram of tensile impact test: (a) side view of Charpy hammer impact and (b) top view of tensile impact apparatus.



Figure 4.3. Installation of dynamic load cells and LVDT on movable guided bases.

# 4.3 Procedure

Two load cells of the range 0-10 lb and 0-100 lb were used for the unfilled and the carbon black-filled natural rubbers, respectively. The load cells and the LVDTs were calibrated in their linear range. The noise (error) in 0-100 lb load cells (load cell under no load) was found to be  $\pm 0.04$  lb (see Fig. 4.4) and the noise (error) in the LVDT was found to be  $\pm 0.1$  in (see Fig. 4.5). A 30-point moving average method was used for data smoothing. As seen from Figs. 4.4 and 4.5, the error in the load cells and LVDT could be reduced to  $\pm 0.005$  lb and  $\pm 0.01$  in, respectively, with data smoothing techniques. For a 5 % error range, the minimum load that could be determined was 0.1 lb and the minimum extension that could be recorded by the LVDT was 0.2 in. When the loads and extensions are above 0.1 lb and 0.2in, the error was less than 5 %.



Figure 4.4. Error band in 0-100 lb load cells.



Figure 4.5. Error band in LVDT.

The ends of the rubber strip specimen were then placed in the grips and the grips tightened adequately in order to prevent slippage of the specimen from the grips. Double-sided duct tape between the rubber specimen and the grips and extrusion of the rubber on the backside of the grip, as shown in Fig. 4.6, prevented slippage. The copper cables connecting the guided base to the slider bar were then made taut enough so that there was a minimum tension in them. The data acquisition system was set up to capture the data. The pendulum (hammer) was dropped from the desired height. Greater heights corresponded to higher strain rates. Upon impact, the hammer pushed the slider bar, which in turn pulled the cables. These cables then pull the guided base and thereby ends of the specimen placed in the grips. The experimental setup is such that a tensile force acts on the specimen and when the force applied was high enough, the specimen failed. Tests in which the specimen broke at the center were considered good and all other tests

are discarded. Four to five tests were conducted at the same drop height in order to get repeatable data. The data recorded by the data acquisition system was processed to get the corresponding stress- strain curves at different strain rates. Any noise recorded was eliminated and the data smoothed out by performing a 30-point moving average.



Figure 4.6. Extrusion of rubber on the backside of grip.

Elongations and forces measured by the LVDT and the load cells, respectively, were converted to extension ratio and stress. The extension ratio,  $\lambda$ , is the ratio of the specimen's current length, L, to the original length, L<sub>o</sub>:

$$\lambda = L/L_o = \frac{\Delta + L_o}{L_o}$$
(4.1)

where  $\Delta$  is the elongation. The engineering strain, e, is thus related to the extension ratio by

$$\mathbf{e} = \lambda - 1 \tag{4.2}$$

The true stress,  $\sigma$ , is the tensile force, F, divided by the current cross-sectional area, A :

$$\sigma = \frac{F}{A} \tag{4.3}$$

Assuming incompressible material (often a good assumption for rubber in tension and shear since the bulk modulus is much greater than the shear modulus) one can relate the engineering stress, s, to the true stress by

$$s = \frac{\sigma}{\lambda} \tag{4.4}$$

# 4.4 Analysis on a linear spring

Simple tension tests were conducted on a linear spring, of known spring constant, in order to check the accuracy of the experiment. The spring mass was  $m_s =$ 9.14\*10<sup>-4</sup> lbs<sup>2</sup>/in and stiffness was k = 1.233 lb/in. The stiffness of the spring was independent of strain rate. Tests were conducted on the spring at different drop heights or initial conditions. Figures 4.7 and 4.8 depict experimental data obtained. The corresponding force-extensions are shown in Figs. 4.9 and 4.10. The spring stiffness was found to be 1.228 lb/in and 1.221 lb/in in Tests 1 and 2, respectively. This was within 1% of the expected value. Thus there was good agreement of the spring constant with its expected value. Calibration of the load cells and LVDTs were done correctly. It must be recalled the LVDTs were calibrated assuming that the gage length of the specimen/spring is 1in. However, the length of spring used for this analysis, was greater than an inch and hence this the extensions recorded by the LVDTs do not start at zero.





(b) Transient displacement.





(a) Transient force.

(b) Transient displacement.

Figure 4.8. Linear spring response for Test 2: (a) Transient force and (b) Transient displacement.



Figure 4.9. Force-extension curve for tensile Test 1 on linear spring.



Figure 4.10. Force-extension curve for tensile Test 2 on linear spring.

Analytical solutions for the transient force and spring extension can be derived by considering the spring as a single degree-of-freedom mass/spring system, as shown in Figs. 4.11(a) and (b). Here the mass of grip is  $m_g$  and the deflection at the grip is u. Due to symmetry of the system, a half model was used for the analysis as shown in Fig.4.11(b).



Figure 4.11. Model of a linear spring: (a) Actual model and (b) Half

The equivalent mass of the spring in the half model is  $m_{eq} = (m_s/2)/3 = m_s/6 = 1.523*10^{-5} \text{ lbs}^2/\text{in}.$ 

The equation of motion for the system in the half model is

$$(\mathbf{m}_{g} + \mathbf{m}_{eq})\ddot{\mathbf{u}} + \mathbf{k}\mathbf{u} = \mathbf{F}(\mathbf{t}) \tag{4.5}$$

Here F(t) is the tensile impact load imparted to the specimen. A third-order polynomial function was fitted to the transient loads F(t) using Microsoft EXCEL. The general form of this equation was

$$F(t) = a_0 + a_1 t + a_2 t^2 + a_3 t^3$$
(4.6)

where  $a_0$ ,  $a_1$ ,  $a_2$  and  $a_3$  were evaluated from the tests. Table 4.3 gives values of  $a_0$ ,  $a_1$ ,  $a_2$  and  $a_3$  for the two different tests.

	Test 1	Test 2
$a_0$ (lb)	0.915	0.488
a <sub>1</sub> (lb/s)	-8.63	37.88
$a_2$ (lb/s <sup>2</sup> )	289.77	-127.95
$a_3 (lb/s^3)$	-888.73	31.89

Table 4.3. Fitting constants for the transient load F(t).

Substituting Equation (4.6) into (4.5) and solving give

$$u = A \sin(\omega_n t) + B \cos(\omega_n t) + C_0 + C_1 t + C_2 t^2 + C_3 t^3$$
(4.7)

where 
$$\omega_n = \sqrt{k/(m_{eq} + m_g)}$$
,  $C_0 = \frac{(a_0 - 2a_3)}{k}$ ,  $C_1 = \frac{(a_1 - 6a_3)}{k}$ ,  $C_2 = \frac{a_2}{k}$ ,  $C_3 = \frac{a_3}{k}$ , and

A and B are determined from the initial conditions. The first two terms indicate the homogenous solution (transient response), while the remaining terms are the particular solution (forced response). Let  $u = u_0$  at t=0 and  $u = \dot{u}_0$  at t=0. These initial conditions are found from the tests.

Using the above expressions for the initial conditions, one gets that

$$\mathbf{A} = \frac{\dot{u}_0 - c_1}{w_n} \tag{4.8}$$

$$\mathbf{B} = \mathbf{u}_0 - \mathbf{c}_0 \tag{4.9}$$

Table 4.4 gives values of C<sub>0</sub>, C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> for the different tests. Calculated values for  $u_0$ ,  $\dot{u}_0$ , A and B are shown in Table 4.5.

	Test 1	Test 2
C <sub>0</sub> (in)	0.539	0.292
C <sub>1</sub> (in/s)	-5.112	22.565
$C_2$ (in/s <sup>2</sup> )	172.59	-76.181
$C_3$ (in/s <sup>3</sup> )	-529.37	18.996

Table 4.4. Coefficients of the particular solutions.

Table 4.5. Initial conditions and coefficients of the homogenous solutions.

	Test 1	Test 2	
u <sub>0</sub> (in)	0.329	0	
$\dot{u}_0$ (in/s)	2.637	0	
A (in)	2.37 E -05	0	
B (in)	-0.00021	-0.000248	

The predicted displacement response for Tests 1 and 2 are shown with the experimental data in Figs. 4.12 and 4.13, respectively. The predicted response consists of the homogenous solution superimposed on the forced response. The experimental data is slightly lower than the expected results at the beginning of the experiment even though the initial conditions were the same. However, the experimental results agree very well with the analytical results when extensions are large, greater than 0.787 in. It was therefore concluded that the experimental data obtained, was good for large

deformations/ strains analysis and that the frictional effects and experimental errors, due to noise and so on, have a negligible effect on the data.





(b) Transient displacement.







(b) Transient displacement.



# CHAPTER V

#### EXPERIMENTAL RESULTS AND DISCUSSIONS

#### 5.1 Quasi-Static Test Results

Engineering and Cauchy stress-extension ratio curves for filled and unfilled NR at strain rates of 0.1 s<sup>-1</sup> are shown in Figs. 5.1 and 5.2, respectively. The stars indicate break points, i.e., extension ratio at break and tensile strength, whereby the specimen breaks in the gage center. Usually the tensile strength is specified in terms of engineering stress, but the cross-sectional area of the tensile specimen reduces significantly and a more accurate representation of the tensile strength of the material is given by the true or Cauchy stress. Both stress measures are given for comparison. The general trend observed from the quasi-static tests on NR was that the strength and stiffness increase with higher amounts of carbon black, up to about 25 phr. Beyond this amount, strength decreases with increasing carbon content while stiffness increases but at a slower rate. The increase in stiffness with percentage of carbon filler has been well documented [33], but the decrease in strength with increasing amounts of carbon filler has not been mentioned as much in the literature. The decrease in tensile strength and fracture strain of NR with increasing carbon black filler could be caused by the carbon black

agglomerates. A large structured filler aggregate has a huge void volume in which the rubber molecules get trapped or occluded during shear mixing [3]. This bound rubber is prevented from crystallizing.



Figure 5.1. Static engineering stress-extension ratio curves of unfilled and filled natural rubber.



Figure 5.2. Static Cauchy stress-extension ratio curves of unfilled and filled natural rubber.

## 5.2 Dynamic Stress-Extension Ratio Curves

High speed tensile tests were conducted on unfilled and filled NR with 25, 50 and 75 phr of N550 carbon black. The 0-10 lb load cell was used for unfilled natural rubber, while the 0-100 lb load cell was used for 25, 50 and 75 phr carbon black-filled NR. Typical force-time and displacement-time data obtained for these tests are shown in Figs. 5.3 and 5.4. When the data from the load cells is compared with that from the LVDT, a lag in the LVDT response can be observed. This lag is due to the initial inertial resistance of the grip and specimen until a constant strain rate can be achieved. At constant strain rate the inertia forces are zero since there is no acceleration. There is also some friction in the system but this is negligibly small. Experience has shown that the material property data is repeatable if the initial transient in the displacement is kept at a minimum, below 0.5 in.

Figures 5.5-5.12 show the dynamic stress-extension ratio curves of each blend of NR. Again both engineering and Cauchy stress are shown for comparison. The static stress-extension ratio curve is also included on these graphs for reference. The stars indicate break points, i.e., extension ratio at break and tensile strength, whereby the specimen breaks in the gage center. For the unfilled NR and some of the 25 phr carbon filled NR, the specimen broke in the grips and break points could not be found. Using dumbbell specimens in the high speed experiments would have prevented this from happening, but the specimen extension can only be measured from the grip travel in the present experimental setup.



Figure 5.3. Data from PCB load cells for 25 phr carbon black filled NR (367 s<sup>-1</sup>).



Figure 5.4. Data from LVDT for 25 phr carbon black filled NR (367  $s^{-1}$ ).



Figure 5.5. Engineering stress-extension ratio curves for unfilled natural rubber.



Figure 5.6. Cauchy stress-extension ratio curves for unfilled natural rubber.



Figure 5.7. Engineering stress-extension ratio curves for natural rubber with 25 phr N550.



Figure 5.8. Cauchy stress-extension ratio curves for natural rubber with 25 phr N550.



Figure 5.9. Engineering stress-extension ratio curves for natural rubber with 50 phr



Figure 5.10. Cauchy stress-extension ratio curves for natural rubber with 50 phr N550.



Figure 5.11. Engineering stress-extension ratio curves for natural rubber with 75 phr N550.



Figure 5.12. Cauchy stress-extension ratio curves for natural rubber with 75 phr N550.

# 5.2 .1 Unfilled Natural Rubber

The dynamic stress-extension ratio curves indicated that stiffness increases with strain rate but beyond 407 s<sup>-1</sup>, the stiffness was almost unchanged, i.e., a "locking" curve was approached. This locking curve was also identified in the unfilled SBR [2,24,25] and was associated with the so-called instantaneous response of the material. The instantaneous response curve represents the material's stiffness without any measurable stress relaxation. The increase in stiffness with increasing strain rate was due to a lack of time for stress relaxation. The static stress-extension ratio curve also appeared to be stiffer than the dynamic stress-extension ratio curves below 277 s<sup>-1</sup> when the extension ratios were greater than 3. This was possibly due to a reduction in the time needed for strain-induced crystallization to occur. Recall that NR is inherently stiff and strong because of strain crystallization. Contrary to the case of SBR, high rates of loading do not necessarily increase the stiffness and strength of NR.

# 5.2 .2 Carbon Black-Filled Natural Rubber

The dynamic stress-extension ratio curves of carbon black-filled NR in Figs. 5.7-5.12 showed similar trends to the unfilled NR in that the modulus increased with increasing strain rate up to a critical value of strain rate. Above the critical strain rate, a locking curve becomes evident for each material. The critical strain rate for locking was 346 s<sup>-1</sup>, 367 s<sup>-1</sup> and 360 s<sup>-1</sup> for the 25 phr, 50 phr and 75 phr carbon-filled NR, respectively. Surprisingly, the strain rates at which locking occurred for the filled natural rubbers were almost the same, about 360 s<sup>-1</sup>. As in the case of the unfilled NR, the static stress-extension ratio curves for 25 phr was stiffer than the dynamic stress-extension ratio curves. Thus a reduction in time for strain-induced crystallization was also playing a role in determining the dynamic properties of 25 phr filled NR. For the 50 phr and 75 phr, the quasi-static tensile stress-extension ratio curve was below the locking curve. Straininduced crystallization was not as prevalent in these materials due to the high amounts of carbon black in them.

Tables 5.1 shows a comparison of the static and highest dynamic Cauchy stress at 300% strain (extension ratio of 4), for the unfilled and filled NR, respectively. A strain of 300% was chosen to reveal the effect of strain-induced crystallization. The static Cauchy stress at 300% strain was about 26% higher than the highest dynamic Cauchy stress at 300% for the 25 phr. This was because the material had enough time to crystallize. It took about 30 sec for the specimen to reach a 300% strain at a strain rate of 0.1 s<sup>-1</sup>, but only 5 ms to reach a 300% strain at a strain rate of 588 s<sup>-1</sup>. Thirty seconds is about five orders of magnitude higher than 5 ms, and it would appear that strain-induced crystallization, as in the case of stress relaxation, needs finite time to become noticeable. The static Cauchy stress at 300% strain were 23% and 28% lower than the highest dynamic stress at 300% for the 50 phr and 75 phr, respectively. Apparently, the percentage of carbon black affected the extent of strain crystallization in NR. Filler reinforcement rather than strain-induced crystallization is more important in highly filled NR. Figure 5.13 gives a comparison of the static and highest dynamic Cauchy stress at 300% strain. The engineering stress is also shown in this diagram for comparison.

	Unfilled NR	NR with 25 phr carbon black	NR with 50 phr carbon black	NR with 75 phr carbon black
Static Cauchy stress at 300% strain (psi) (strain rate at 0.1s <sup>-1</sup> )	503	3,800	8,856	10,060 <sup>(2)</sup>
Highest dynamic Cauchy stress at 300% strain (psi)	1,500	3,000	11,500	14,500 <sup>(2)</sup>

Table 5.1. Comparison of static and highest dynamic Cauchy stress at 300% strain.

(2) Extrapolated value



Figure 5.13. Comparison of static and highest dynamic Cauchy and engineering stress at 300% strain.

Break points, indicating tensile strength and extension ratio at break at constant strain, could be obtained for most of the filled NR tests. This was because the carbon black filler was toughening the material held in the grip. A comparison of the Cauchy tensile strength during static and dynamic loading is shown in Table 5.2. The break point for the lower strain rate could not be determined since a constant strain rate until break could not be maintained in the tests. No dynamic Cauchy tensile strength was obtained for the unfilled NR due to the fact that the specimen broke in the grip instead of the center of gage area. For the 25 phr and 50 phr carbon black-filled NR, the highest dynamic Cauchy tensile strength was below the static Cauchy tensile strength. However, the highest dynamic Cauchy tensile strength was about double that of the static Cauchy tensile strength for the 75 phr carbon-filled NR. The high content of carbon black filler in the 75 phr carbon filled NR had evidently changed the morphology of NR to the point that the material was not undergoing any substantial strain-induced crystallization. The dynamic Cauchy tensile strength of the 75 phr filled NR was higher than the static value because of filler reinforcement. Another interesting observation from Table 5.2 was that the highest dynamic Cauchy tensile strength increased from 25 phr to 75 phr carbon black filler in the NR, while the opposite trend was observed for the static Cauchy tensile strength. Thus carbon black filler can increase the tensile strength of NR by filler reinforcement but only at high rates of loading. This conclusion is very important in predicting damage of tire treads which experience high rates of loading.

	Unfilled NR	NR with 25 phr carbon black	NR with 50 phr carbon black	NR with 75 phr carbon black
Static tensile strength (psi) (strain rate at 0.1s <sup>-1</sup> )	11,104	22,638	16,863	8,856
Highest dynamic tensile strength (psi)	<b>**</b> (1)	12,974	14,538	17,342

Table 5.2. Comparison of static and highest dynamic Cauchy tensile strength.

(1) Test data could not be found.

# 5.3 Mullins' Effect

When carbon black-filled rubber vulcanizates were stretched and then allowed to retract (unloaded), subsequent extensions to the same strain required a lower force. Most of the softening occured during the first few cycles. After 3-4 cycles, a steady state hysteresis was approached. The phenomenon of stress softening is known as Mullins' Effect [51], which has been documented and studied by many researchers at material strain rates below 1 s<sup>-1</sup>. Stress softening has been attributed to the destruction of filler networking, i.e., the breakdown of weak bonds between the filler particles within aggregates and between filler particles and rubber molecules. The area within the hysteresis loop gives energy dissipated per cycle. This includes the frictional losses and energy absorbed in the destruction of filler bonding. As proposed by Dannenberg [52, 53, 54], molecular slippage or sliding of elastomer segments across the filler interface also causes stress-softening. An experiment was done to investigate the Mullins' effect at high loading rates using the Charpy tensile impact apparatus.

Cyclic loading was imposed on NR with 75 phr of N550 carbon black by hand pushing-pulling the slider bar shown in Fig. 4.2 (a) between fixed distances. The resulting hysteresis loops for the material and the strain rate associated with loading/unloading event are given in Fig. 5.7. Ideally one would like to control the strain rate during loading/unloading, but this could only be achieved approximately using the simple tensile impact apparatus. Four hysteresis loops at loading/unloading strain rates ranging from 6-13.7 s<sup>-1</sup> were obtained after much trial-and-error. The data indicated a Mullins' effect as well as a permanent extension ratio of about 1.25 or 25% strain after the first cycle. The permanent strain appeared to be fixed for the given range of extension ratio (1-1.8) and this indicated that the permanent strain was associated with the stretch-related damage discussed earlier, i.e., the destruction of filler networks. A stable hysteresis was observed during the fourth cycle. It can be concluded from this study that the Mullins' effect, which has been observed at quasi-static strain rates (less than  $1 \text{ s}^{-1}$ ), can occur at rates on the order of  $10 \text{ s}^{-1}$ . However, cyclic tests at higher strain rates, on the order of 100 s<sup>-1</sup> or even 1,000 s<sup>-1</sup>, would have to be conducted in order to understand how loading rates can affect damage mechanisms that produce cyclic stress softening or the Mullins' effect. This will be addressed in future research.



Figure.5.14. Engineering stress-extension ratio curves depicting Mullins' effect in natural rubber with 75 phr N550.



Figure.5.15. Cauchy stress-extension ratio curves depicting Mullins' effect in natural rubber with 75 phr N550.

# CHAPTER VI

#### STRAIN RATE EFFECT ON STRAIN-INDUCED CRYSTALLIZATION

The main strengthening mechanism in natural rubber is strain-induced crystallization. As discussed in the previous chapter, strain-induced crystallization appears to be a time dependant phenomenon, which is suppressed at higher rates of loading, and high amounts of carbon black fillers impedes strain-induced crystallization. In order to study the effect of increasing strain rates on the mechanism of strain-induced crystallization, more experiments were conducted on only the unfilled natural rubber. Due to the absence of fillers in unfilled natural rubber, the effect of carbon black fillers on strain-induced crystallization was eliminated.

Figures 6.1-6.3 show the variation of Cauchy stress with strain rates at 100 %, 200 % and 300 % strain, respectively, in the unfilled NR. It can be observed from Fig. 6.1 that as the strain rate increased the Cauchy stress values first decreased between  $0.1 \text{ s}^{-1}$  to 157 s<sup>-1</sup> and then increased progressively with strain rates above 157 s<sup>-1</sup>. The same trend is observed at 200 % and 300 % strain in Figs. 6.2 and 6.3.



Figure 6.1. Variation of Cauchy stress at 100% elongation with strain rate in unfilled NR.



Figure 6.2. Variation of Cauchy stress at 200% elongation with strain rate in unfilled NR.



Figure 6.3. Variation of Cauchy stress at 300% elongation with strain rate in unfilled NR.

It is apparent from the above figures that the NR underwent a transition point whereby there was perhaps not enough time for strain-induced crystallization. Experiments were conducted recently (September, 2005) using a servo-hydraulic MTS machine to examine the behavior of natural rubber in the strain rate range of 0.1 s<sup>-1</sup> to 100 s<sup>-1</sup>. This is the range for which data was not obtained using the Charpy impact apparatus. Figure 6.4 shows the full stress-extension ratio curves at strain rates in the range 0.1 s<sup>-1</sup> - 40 s<sup>-1</sup>. It is observed that the stiffness increased with increasing strain rate between 1 s<sup>-1</sup> and 40 s<sup>-1</sup>. However the material at 0.1 s<sup>-1</sup> is stiffer than it is at 1, 5 and 10 s<sup>-1</sup>.

Figure 6.5 shows the variation of the Cauchy stress with strain rate at 40 % elongation in the unfilled NR plotted together with the Charpy tensile impact data acquired between March-April, 2005, and the Cauchy stress-extension ratio at  $0.1 \text{ s}^{-1}$ 

from an INSTRON machine obtained in January, 2005. Notice that the Cauchy stress at 40% strain and  $0.1 \text{ s}^{-1}$  strain rate from the INSTRON machine in January, 2005 and the MTS machine in October, 2005 do not match each other. The material became stiffer after 9 months despite the fact that it was kept in a refrigerator. The material had aged.

While comparison of the data obtained in October, 2005, with data from Jan-March, 2005, was not successful, comparison of the aged natural rubber alone can be done. Figure 6.6 shows the variation of the Cauchy stress at 40%, 100% and 180% strain with strain rate. It can be observed that Cauchy stress increased with increasing strain rate from 0.1 s<sup>-1</sup> to 5 s<sup>-1</sup>, but then decreased as the strain rate increased in the strain rate region of 5 s<sup>-1</sup> to 10 s<sup>-1</sup>. For strains greater than 10 s<sup>-1</sup>, the Cauchy stress increased with increasing strain rate. The decrease in stress between 5 s<sup>-1</sup> to 10 s<sup>-1</sup> is more dominant at higher elongations. It appears to be related to strain-induced crystallization, which occurs at higher strains.



Figure 6.4. Behavior of unfilled natural rubber at low strain rates.



Figure 6.5. Strain induced crystallization and stress relaxation in unfilled NR at 40% strain.



Figure 6.6. Strain induced crystallization and stress relaxation in aged unfilled NR.

# CHAPTER VII

### CONCLUSIONS

High speed tensile tests were conducted on unfilled and 25 phr, 50 phr, 75 phr carbon black-filled natural rubber using a Charpy tensile impact apparatus. It was shown that the modulus of the stress-extension ratio curves increased with increasing strain rate up to about 407 s<sup>-1</sup>, 367 s<sup>-1</sup>, 346 s<sup>-1</sup> and 360 s<sup>-1</sup> for unfilled, 25phr, 50phr and 75 phr filled NR, respectively. Above these strain rates, the unfilled and filled NR stress-extension ratio curves remained unchanged. The dynamic stress-extension ratio curves from these tests were compared to those obtained in quasi-static tests using an electromechanical INSTRON machine. The general shape of the dynamic stress-extension ratio curves was different from those of the quasi-static tests. The initial modulus (modulus at low strain) of the dynamic stress-extension curves was very high and then decreased with extension ratio, while that of the static curve was initially low and increased with increasing extension ratio. Dynamic stress-extension curves also did not have the very sharp upturn at break, which was characteristic of strain crystallizing natural rubber under quasi-static loading.

The 25 phr carbon black-filled NR was actually stiffer at large strains (greater than 300%) under quasi-static loading than it was under high rates of loading. This was due to insufficient time for strain-induced crystallization in the material at high strain rates. When the static stress at 300% strain was compared to the highest dynamic stress at 300% strain, it was found to be 26% higher for the 25 phr NR, 23% lower for the 50 phr NR and 28% lower for the 75 phr NR. This indicated that high amounts of carbon black hindered strain-induced crystallization, which was becoming less evident at higher rates of loading. This conclusion can be further substantiated by noting that even the static tensile strengths of the 50 phr and 75 phr carbon black-filled natural rubbers.

The highest dynamic tensile strengths for unfilled, 25 phr and 50 phr carbon blackfilled NR were found to be lower than those from the static tensile tests for these materials. This again indicated that during high rates of loading, natural rubber may not have time to undergo strain-induced crystallization. It would appear that strain crystallization needs a finite time to occur. In contrast to the 25 phr and 50 phr carbonblack filled NR, the highest dynamic tensile strength for the 75 phr carbon black-filled NR was greater than that from the static tensile test. Thus very high amounts of carbon black will impede strain-induced crystallization and the dynamic tensile strength of a highly filled NR is determined primarily from filler reinforcement.

One of the main shortcomings of the current Charpy impact apparatus was that the LVDT could only measure grip displacement and hence the extension of the specimen held between the grips. This restricted the tensile specimens to be strips instead of dumbbells. The extensions in the gage section of a dumbbell specimen could not be

measured by the LVDTs. Dumbbell or a dogbone shape of specimens is preferred over a strip specimen because they prevent the specimen from breaking in the grip. In an ongoing effort to improve the experimental setup, a high speed camera was purchased to measure the extensions of the specimens, i.e., to be used as a video extensometer. Future work is planned to analyze the effect of different filler types on the high strain rate properties of natural rubber. A similar study will also be carried out to investigate the effect of fillers on high strain rate properties of SBR, which is not a strain crystallizing rubber.

# REFERENCES

[1] Vickers, H.H. and Robison, S.B., "Measurements of tread motions and application to tire performance," in the Proceedings of the International Rubber Conference, Washington DC, Nov 8-13, 1959, pp. 128-141.

[2] Bekar, I., Hoo Fatt, M. S. and Padovan, J., "Deformation and Fracture of Rubber under Tensile Impact Loading," Tire Science and Technology Journal, Vol. 30, No. 1, 2002, pp. 45-58.

[3] Gent, A. N. (editor), "Engineering with Rubber: How to Design Rubber Components," 2<sup>nd</sup> Edition, Hanser Publishers, Munich, 2001.

[4] Bateman, L., "The Chemistry and Physics of Rubber-like Substances", MacLaren and Sons Ltd., London, 1963.

[5] Kelly, J. M., "Earthquake Resistant Design with Rubber," Springer-Verlag, London, 1997.

[6] Duncan, J., "Dynamic Mechanical Analysis Techniques and Complex Modulus," in Mechanical Properties and Testing of Polymers: An A-Z Reference, edited by GM Swallowe, Kluwer Academic, Dordrecht, 1999.

[7] Yang, L. M., Shim V. P. W. and Lim C. T., "A visco-hyperelastic approach to modeling the constitutive behavior of rubber", International Journal of Impact Engineering, Vol. 24, 2000, pp. 545-560.

[8] Williams, M. L., Landel, R. F. and Ferry, J. D., "The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids", J. Am. Chem. Soc., Vol. 77, 1955, pp. 3701-3707.

[9] Smith, T. L., "Dependence of the ultimate properties of GR-S rubber on strain rate and temperature", Journal of Polymer Science, Vol. 32, 1958, pp. 99-113.

[10] Nadai, A. and Manjoine, M. J., "High-Speed Tension Tests at Elevated Temperatures", American Society for Testing Materials, Proc. of the 43<sup>rd</sup> Annual Meeting, Atlantic City, June 24-28, Vol. 40, 1940, pp. 822-837.

[11] Villars, D. S., "Ultra speed tensile strength of rubber and synthetic elastomers", J. Appl. Phys., Vol. 21, 1950, pp. 565-43.

[12] Dogadkin B. A. and Sandromirski D. M., "Effect of temperature and the rate of stretching on the tensile strength of vulcanizates", Rubber Chem. And Technology, Vol. 25, 1952, pp. 50-5.

[13] Greensmith, H. W., "Rupture of rubber: effect of rate of extension in tensile tests", Journal of Applied Polymer Science, Vol. 3, No. 8, 1960, pp. 175-182.

[14] Dannis, M. L., in A. G. H. Dietz and F. R. Eirich, eds, "High speed testing", Vol. 3., Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1962, pp. 35.

[15] Kainradl, P. and Handler, F., "Investigation on notch sensitivity of vulcanisates.", Kaut. Un Gummi, Vol. 12, No. 9, 1959, pp. 239-46.

[16] Rao, S., Shim, V. P. W. and Quah, S. E., "Dynamic Mechanical Properties of Polyurethane Elastomers using a Nonmetallic Hopkinson Bar," J. Applied Polymer Science, Vol. 66, 1997, pp. 619-631.

[17] Shim, V. P. W., Yang, L. M., Lim, C. T. and Law, P. M., "A Visco-Hyperelastic Constitutive Model to Characterize both Tensile and Compressive Behavior of Rubber," J. Applied Polymer Science, Vol. 92, 2004, pp. 523-531.

[18] Chen, W., Lu, F., Frew, D. J. and Forrestal, M. J., "Dynamic Compressive Testing of Soft Materials," Journal of Applied Mechanics, Vol. 69, 2002, pp. 214-223.

[19] Song, B. and Chen, W., "One-Dimensional Dynamic Compressive Behavior of EPDM Rubber," J. Eng. Mat. Tech., Vol. 125, 2003, pp. 294-301.

[20] Song, B. and Chen, W., "Dynamic Compressive Behavior of EPDM Rubber Under Nearly Uniaxial Strain Conditions," Journal of Engineering Materials and Technology, Vol. 126, 2004, pp. 213-217.

[21] Song, B. and Chen, W., "Dynamic Stress Equilibrium in Split Hopkinson Pressure Bar Tests on Soft Materials," Experimental Mechanics, Vol.44, No. 3, 2004, pp. 300-312.

[22] Quintavalla, S. J. and Johnson, S. H., "Extension of the Bergstrom-Boyce model to high strain rates," Rubber Chem Tech., Vol. 77, No. 5, 2004, pp. 972-981.

[23] ASM Handbook, Mechanical Testing and Evaluation, Vol. 8, H. Kuhn and D Medlin (editors), Materials Park, OH, 2000.

[24] Hoo Fatt, M.S., Bekar, I., and Padovan J., "Tensile Impact of SBR – Rate-Dependent Deformation and Fracture Characteristics," presented at EUROMECH Colloquium on Constitutive Equations for Polymer Micro-composites: on the Border of Mechanics and Chemistry, Vienna, Austria, July 15-17, 2002.

[25] Hoo Fatt, M.S. and Bekar, I., "High-Speed Testing and Material Modeling of Unfilled Styrene Butadiene Vulcanizates at Impact Rates," Journal of Materials Science, Vol. 39, No. 23, 2004, pp. 6885-6899.

[26] Bruzzone, M., Corradini, G., De Chirico, A., Guiliani, G., and Modini, G., "Branching and molecular weight distribution in 1, 4-cis-polyisoprenes and effect on the dynamic properties", in the Proceedings of the 4<sup>th</sup> Int. Synth. Rubb. Symp., London, Sep 30 – Oct 2, 1969, pp. 83-87.

[27] Angulo-Sanchez, J.L. and Caballero-Mata, P., "Long chain branching in natural Hevea rubber - determination by gel permeation chromatography", Rubb. Chem. Technol., Vol. 54, No.1, 1981, pp. 34-41.

[28] Mark, J. E., (editor), "Physical properties of polymers handbook", American Institute of Physics Press, Woodbury, New York, 1996.

[29] Katz, J.R., "Roentgen spectrographs of rubber under different degrees of elongation. A new method for studying rubber and its extensibility", Chemiker-Zeitung, Vol. 49, 1925, 353-354.

[30] Acken, M.F., Singer, W.E. and Davey, W.P., "X-ray study of rubber structure", Industrial and Engineering Chemistry, Vol. 24, 1932, 54-57.

[31] Bekkedahl, N. and Wood, L.A., "Crystallization of vulcanized rubber", Industrial and Engineering Chemistry, Vol. 33, 1941, 381-384.

[32] Bhowmick, A.K., Kuo, C.C., Manzur, A., MacArthur, A. and McIntyre, D., "Properties of cis- and trans- Polyisoprene Blends", Journal of Macromol. Sci., Phys. Ed. Vol. 25, 1986, 283-306.

[33] Roberts, A.D (editor), "Natural Rubber Science and Technology" Oxford University Press, Oxford, 1988.

[34] Donnet, J. B and Voet, A., "Carbon Black, Physics, Chemistry and Elastomer Reinforcement", Marcel Dekker Publishers, New York, 1976.

[35] Kraus, G. (editor), "Reinforcement of Elastomers", Wiley Intersci., New York, 1965.

[36] Gregory, M. J., "Selection of carbon black fillers for natural rubber springs", Rubber Chem. Technol., Vol. 52, No. 5, 1979, pp. 996-1007.

[37] Hess, W.M and Ford, F.P., "Microscopy of Pigment-Elastomer Systems", Rubber Chem. Technol., Vol. 36, 1963, pp.1175-1229.

[38] D 3849, Annual Book of ASTM Standards, Vol. 09.01, 1990, p.630.

[39] Donnet, J. B., Bansal, R. C. and Wang, M. J. (editors), "Carbon Black", 2<sup>nd</sup> Edition, Marcel Decker Publishers, New York, 1993.

[40] Smallwood, H.M., "Limiting Law of the Reinforcement of Rubber", J. Appl. Phys., Vol. 15, 1944, pp.758-766.

[41] Guth, E., "Theory of Filler Reinforcement", Rubber Chem. Technol., Vol. 18, 1945, pp.596-604.

[42] Gehman, S.D., in "Reinforcement of Elastomers", G. Kraus ed., Wiley Intersci., New York, 1965.

[43] Lee, D.J and Donovan, J.A., "Microstructural Changes in the Crack Tip Region of Carbon-Black-Filled Natural Rubbers", Rubber Chem. Technol., Vol. 60, 1987, pp.910-923.

[44] Eirich, F.R., in "Les Interactions entre les Elastomeres et les Surfaces Solides Ayant une Action Renforcante", p. 15, Colloques Internationaux du CNRS, Paris, 1975.

[45] Liu, H., Lee, R.F. and Donovan, J.A., "Effect of Carbon Black on the J-Integral and Strain Energy in the Crack Tip Region in a Vulcanized Natural Rubber", Rubber Chem. Technol., Vol. 60, 1987, pp.893-909.

[46] Goldberg, A., Lesuer, D.R. and Patt, J., "Fracture Morphologies of Carbon-Black-Loaded SBR subjected to Low-Cycle, High-Stress fatigue", Rubber Chem. Technol., Vol. 62, 1989, pp.272-287.

[47] ISO 2393: Rubber Test Mixes – Preparation, Mixing and Vulcanization – Equipment and Procedures, 2<sup>nd</sup> Edition, 1994.

[48] Annual Book of ASTM Standards, Vol. 09.01, 1998.

[49] ASTM D 3182-89: Standard Practice for Rubber - Materials, Equipment and procedures for Mixing Standard Compounds and Preparing Standard Vulcanized Sheets, 1994.

[50] ASTM D 3183-84: Standard Practice for Rubber - Preparation of Pieces for Test Purposes from Products, 1998.

[51] Mullins L, "Effect of Stretching on Properties of Rubber," J. Rubber Research, Vol. 16, 1947, pp. 275-289.

[52] Dannenberg, E.M., Trans. Inst. Rubber Ind., Vol. 42, T26, 1966.

[53] Dannenberg, E.M., "The Effects of Surface Chemical Interactions on the Properties of Filler-Reinforced Rubbers", Rubber Chem. Technol., Vol. 48, 1975, pp.410-444.

[54] Dannenberg, E.M. and Brennan, J.J., "Strain Energy as Criterion for Stress-Softening in Carbon Black Filled Vulcanizates", presented at a meeting of Rubber Division, ACS, Philadelphia, Oct 20-22, 1965.