

# EFFECTS OF CARBON BLACK TYPE ON BREATHABLE BUTYL RUBBER MEMBRANES

P. Threepopnatkul, D. Murphy, and J. Mead  
Department of Plastics Engineering  
University of Massachusetts Lowell  
Lowell, MA

W. Zukas\*  
U.S. Army RDECOM  
Natick Soldier Center  
Natick, MA

## ABSTRACT

This study addresses the formulation effects of carbon black type and carbon black loading on the physical properties of electrospun butyl rubber nonwoven membranes. These membranes are envisioned as a potential breathable barrier layer in chemical and biological (CB) protective garments. The advantages of an electrospun crosslinked elastomer system, when compared to similarly prepared thermoplastics, are increased flexibility, durability, and chemical resistance. The porosity and surface area of these membranes are directly related to the water vapor transmission, air flow resistance, aerosol resistance, and the transport of chemical vapors. The barrier properties will be affected by the ability to control pore sizes, fiber diameter, permeability, and physical properties through formulation and process variables. Experimental results reveal that fiber diameter decreased with decreasing carbon black particle size and increasing carbon black structure. Density of the electrospun mats decreased with smaller particle size and higher structure. Decreasing carbon black particle size and increasing structure showed increased stress at break, ultimate elongation and modulus of the membranes. Good dispersion of smaller carbon black size and higher carbon black structure lead to decreased electrical resistance and increased ultimate strength.

## 1. INTRODUCTION

Electrospun fibers have broad application in traditional nonwovens markets. Electrospun fibers are being considered for a variety of applications where their unique properties contribute to product functionality. These properties include high surface area, small fiber diameter, potential to incorporate active chemistries, thinner membranes, high permeability, and reduced weight. One possible application of electrospun nonwoven mats is for protective clothing. The materials for protective clothing applications must be selected such that they protect the user from exposure, while providing comfort to the wearer. The ability to transmit water vapor, flexibility, and stretchability are all garment attributes that

increase user comfort. The resulting small pore sizes of electrospun fabrics coupled with high porosity indicates that the materials would provide good resistance to chemical aerosols; while still permitting significant water vapor transport. (Schreuder-Gibson et al., 2003).

While commercially available thermoplastic based porous membranes provide good breathability, they lack flexibility and the ability to stretch that can be provided by elastomeric materials. On the other hand, butyl rubber films have the ability to stretch and are utilized in chemical protective systems (Wilusz and Hassler, 1992), but do not provide breathability. There is a need for new materials offering a combination of stretch, breathability, and chemical resistance. A number of approaches have been investigated, including urethane membranes, thermoplastic elastomer films (Xu et al., 2002; Satas et al., 1965; Lomax, 1985; Lomax, 1990; and Groitzsch and Fahrbach, 1986), and thermoplastic elastomer membranes manufactured via the electrospinning process (Schreuder-Gibson et al., 2003; and Gibson et al., 2001). Research has been performed establishing the effects of processing parameters: voltage, viscosity, distance to target, etc., on the structure of the electrospun mat (Deitzel et al., 2001). The most challenging concerns are the ability to control pore sizes, fiber diameter, permeability, and mechanical properties.

Recently, the electrospinning process has been applied to thermosetting elastomers for developing nonwoven membranes with a micro porous structure for use in dynamic applications (i.e. stretchable), such as breathable, stretchable protective clothing (Viriyabanthorn, 2004). For electrospun thermosetting elastomers, compound variables, such as filler loading, which can also influence the structure, have been investigated (Viriyabanthorn et al., 2006). Carbon black is known to play a large role in the properties of a rubber compound, acting as a reinforcing filler. In general, the properties of the filled vulcanizate depend on the following carbon black characteristics: the particle size, its structure, and the loading level of carbon black. The particle size is inversely related to the specific surface area of the carbon black available to interact with the

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1. REPORT DATE <b>01 NOV 2006</b>	2. REPORT TYPE <b>N/A</b>	3. DATES COVERED -			
4. TITLE AND SUBTITLE <b>Effects Of Carbon Black Type On Breathable Butyl Rubber Membranes</b>		5a. CONTRACT NUMBER			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S)		5d. PROJECT NUMBER			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Department of Plastics Engineering University of Massachusetts Lowell</b>		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>See also ADM002075., The original document contains color images.</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>UU</b>	18. NUMBER OF PAGES <b>8</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

elastomer. The strength of a rubber compound generally increases with increasing surface area (decreasing particle size). Structure describes the number of particles fused together to form an aggregate, as well as the shape of the aggregate. Structure can influence strength and wear, although the relationships can often be complex and dependent on the carbon black loading (Dick, 2001; Kraus, 1978). Generally, failure properties of the compound, for example, tensile strength, tear strength, and abrasion resistance are affected by loading and surface area, while non-failure properties, such as viscosity, shrinkage and modulus are usually affected by loading and structure.

The effects of carbon black type on the properties of electrospun butyl membranes were evaluated in this study and the results are presented in the following sections.

## 2. EXPERIMENTAL

### 2.1 Materials

The effects of carbon black type were evaluated in this study using a standard sulfur cured butyl rubber compound (**Table 1**). Eight different types of carbon black, each with different particle size and structure, were used at loadings of 25, 30, and 40 parts per hundred rubber (phr).

**Table 1.** Butyl Rubber Formulation

Material	phr*
Elastomer (Exxon Butyl 268)	100
Processing Aid (VANFRE AP-2)	2
Activator-metal oxide (Zinc oxide)	5
Activator-fatty acid (Stearic Acid)	1
Vulcanizing Agent (Sulfur)	2
Accelerator (Methyl Tuads)	1
Accelerator (Captax)	0.5
Carbon Black	study

\* phr = parts per hundred parts rubber

The different carbon blacks consisted of, N-134, N-220, N-234, N-330, N-339, N-550, N-660 (Cabot Corporation) and N990 (Vanderbilt Company). The properties of the carbon blacks are shown in **Table 2**. The carbon blacks N-134, N-339 and N-550, were selected to have similar structure, as shown by their similar values of dibutyl phthalate (DBP) absorption. The carbon black N-990 has the lowest DBP number of the blacks, indicating very little particle aggregation or structure. Nitrogen surface area (BET  $N_2SA$ ) is a measure of the amount of nitrogen that can be adsorbed on a given mass of carbon black, giving an indirect characterization of carbon black particle size. Carbon black N-990 has the

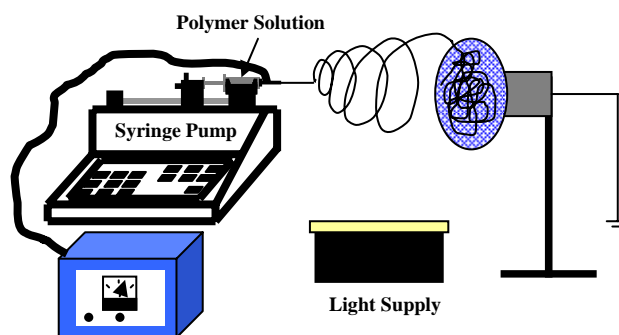
largest particle size of the carbon blacks and hence has lowest surface area.

**Table 2:** Carbon Black Grades

CB grade	BET $N_2SA$ $m^2/g$	DBP $cm^3/100g$	CDBP $cm^3/100g$	Av. Particle Size nm
N134	145	122	103	20-25
N234	125	125	109	24-33
N220	116	114	99	24-33
N339	95	121	104	28-36
N330	83	101	85	28-36
N550	41	122	81	39-55
N660	36	91	73	49-73
N990	9	38	34	250-350

### 2.2 Compounding and Electrospinning

Compounds were mixed at room temperature in a torque rheometer, first masticating the butyl rubber, then followed by dispersion of the carbon black and the addition of the other components. The rubber compound was then dissolved in tetrahydrofuran to a fixed solution viscosity. Electrospinning was carried out using a metering pump connected to a syringe. A high DC power supply was used to charge the polymer solution (12 kV) contained in the syringe and the membrane was collected on a rotating aluminum plate target. Electrospun membranes were dried at room temperature, then heated to 60°C to remove any residual solvent. The samples were then cured in an air oven at 171°C. A schematic of the electrospinning system used in this research is shown in **Figure 1**. The flow rate of the polymer solution was controlled at 1 ml/min. Thicknesses of the butyl rubber membranes varied from approximately 0.2-1.0 mm.



**Figure 1.** Schematic of the electrospinning system.

### 2.3 Characterization

The morphology of the electrospun butyl nonwoven mats was studied by high resolution scanning electron microscopy (SEM) (AMRAY 1400 SEM, with a  $LaB_6$

filament) operating at an accelerating voltage of 10 kV. All specimens were sputter-coated with gold prior to SEM. The fiber diameter was measured on the SEM images using GAIA Blue software.

Density measurements were made in accordance to ASTM D-792. Specimen weight was measured in air and then in water including the wire and sinker. The specific density was then calculated using the following equation (1)

$$\text{Specific density} = a/(a+w+b) \quad (1)$$

where a is the mass of specimen in air, b is the mass of specimen, sinker, and wire in water, and w is the mass of sinker and wire in water.

The electrical conductivity of the electrospinning solution was measured using two probes with an electrometer (Fluke 187/189, resistance 0 to 500 Mega Ohms). The solution with various carbon black types was tested for resistance using a fixed distance between the two probes. Afterwards, the resistance (R,  $\Omega$ ) values were converted to resistivity ( $\rho$ ,  $\Omega\cdot\text{m}$ ), using equation (2),

$$\rho = RA/d \quad (2)$$

where A is the cross-sectional area perpendicular to the direction of the current, d is the distance between two points over which the voltage was measured. Electrical conductivity, used to specify the electrical character of materials can be calculated using equation (3)

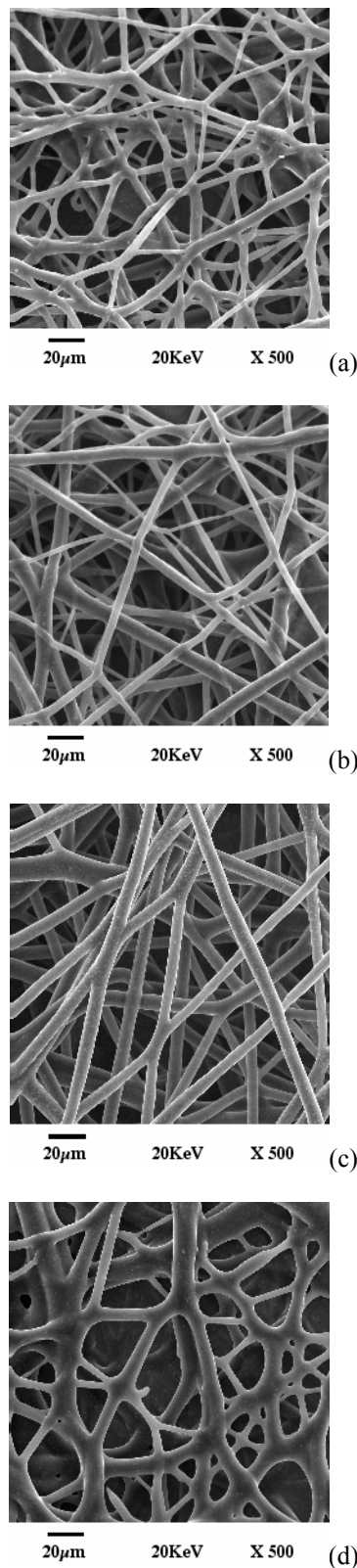
$$\sigma = d/\rho \quad (3)$$

Tensile testing was performed on a universal testing machine (Instron Model 4400) with a crosshead speed of 5 cm/min. Specimens were prepared using a half scale ASTM D412 die. The crosshead displacement was used to measure the strain.

### 3. RESULTS AND DISCUSSION

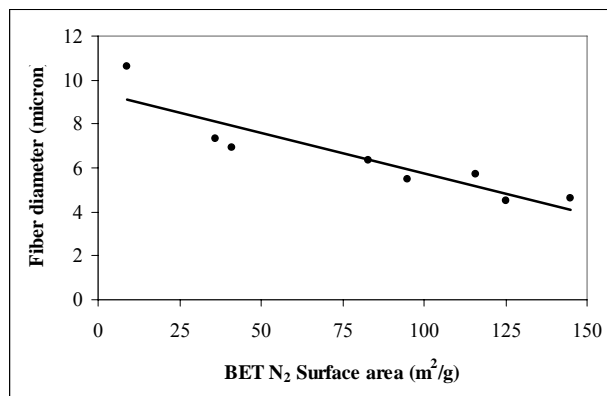
#### 3.1 Fiber Morphology

Morphology of the prepared membranes was studied with high resolution scanning electron microscopy (SEM). An example of prepared membranes at 25 phr carbon black is shown in the SEM micrographs in **Figure 2**. Dispersion of the carbon black in the fibers was investigated with transmission electron microscopy (TEM). The electrical conductivity of the electrospinning solution, membrane density, mechanical tensile properties, and electrical properties of the cured membranes were also measured.



**Figure 2.** SEM of prepared butyl rubber membranes with two different carbon blacks at 25 phr: (a) N-134, (b) N-220, (c) N-550, and (d) N-990

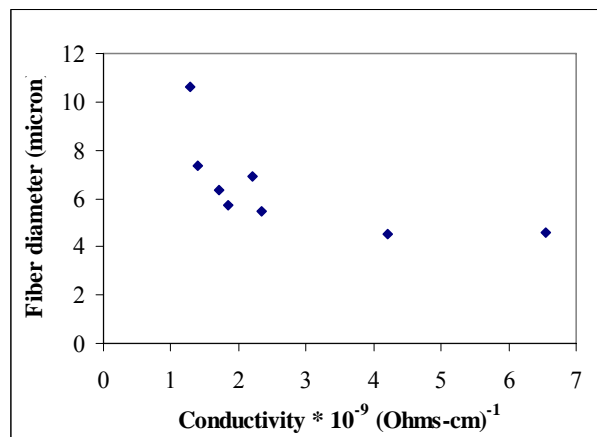
**Figure 3** shows the average fiber diameter of electrospun butyl membranes as a function of carbon particle size for 25 phr loaded samples. The fiber diameter increases with decreasing BET N<sub>2</sub> surface area (increasing particle size). A similar increase in fiber diameter was observed for decreasing carbon structure as indicated by lower DBP oil absorption.



**Figure 3.** Effect of carbon black particle size on fiber diameter at 25 phr carbon black.

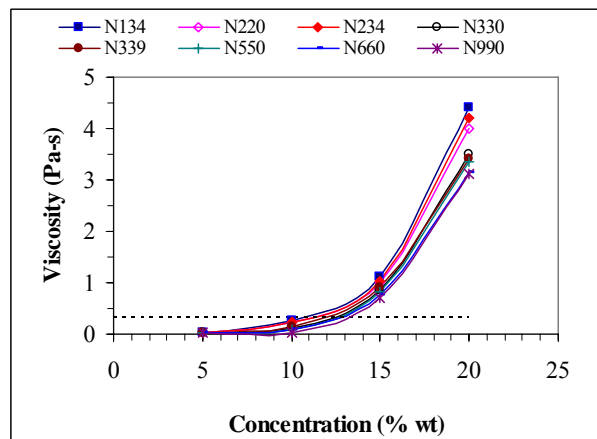
There are two possible reasons to explain the effect of carbon black type on fiber diameter. Since carbon black is a conductive filler, one explanation for the relationship between fiber diameter and carbon black types is the electrical conductivity of the solution. It has been reported that the conductivity of the solution has an influence on the whipping frequency of the electrospinning jet (Hohman et al., 2001). From their prediction, using an electrodynamic model to explain the electrospinning phenomenon, there should be a decrease in fiber diameter with increasing solution conductivity.

**Figure 4** presents the effect of carbon black type on the electrical conductivity of the rubber solution in this study. As predicted, the fiber diameter decreases with increasing conductivity, but in a nonlinear fashion. Smaller particles lead to better conductivity, assuming aggregate length and loading remain constant. Structure of the carbon black also influences conductivity. High structure carbon blacks have many particles, which make up large aggregate sizes with considerable branching. A higher structure with a large amount of long branches will increase the chances of aggregates touching each other, providing conductive pathways. Therefore, adding smaller particle size and higher structure carbon black in the butyl rubber compound increases the conductivity of polymer solution, and thus results in decreased fiber size of the electrospun butyl rubber nonwoven mats.



**Figure 4.** Effect of solution conductivity on fiber diameter.

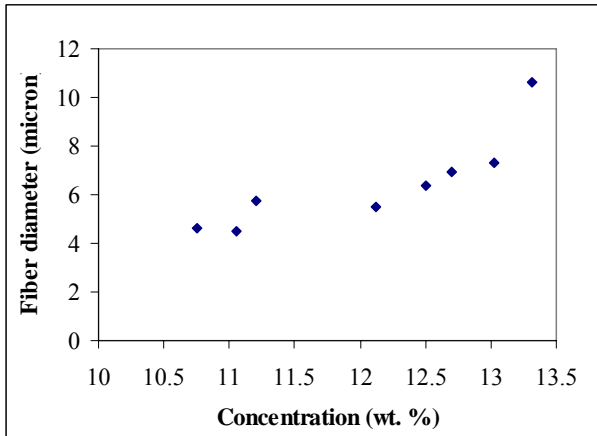
During the experiments in this study, the solution viscosity for electrospinning was kept at a constant value (0.33 Pa-s). Because carbon black type will have an effect on compound viscosity, the results shown in **Figure 4** were obtained for slightly different solution concentrations. As shown in **Figure 5**, if the concentration of the compound in the starting solution is kept constant, then the starting solution viscosity would vary. Higher structure and smaller particle size carbon black lead to a decrease in solution concentration to maintain the same solution viscosity.



**Figure 5.** Viscosity of CB/Butyl rubber solutions as function of polymer concentration for different carbon black types.

Solution concentration is known to influence the fiber morphology with fiber diameters decreasing as the polymer solution concentration decreases (Doshi and Reneker, 1995; Deitzel et al., 2001). As shown in **Figure 6**, the fiber diameter shows the expected decrease as the starting solution concentration decreases. Both the electrical conductivity and concentration of solution play an important role in determining the fiber formability and diameter. Higher structure and smaller particle size of

carbon black would lead to an increase in electrical conductivity and result in a decrease in concentration to keep the same solution viscosity. These two effects would thus be expected to yield smaller fibers. The linear relation between fiber diameter and concentration, however, leads to the premise that concentration may be more critical than conductivity.



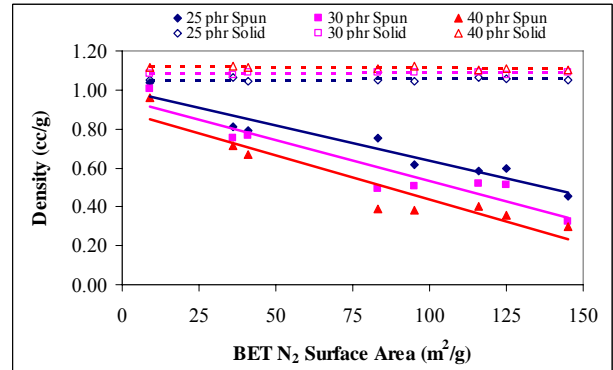
**Figure 6.** Effect of solution concentration on fiber diameter of butyl rubber electrospun nonwoven mats.

The effect of carbon black type and loading in the butyl rubber compound on fiber morphology can also be seen in the density and density ratio of electrospun mats as shown in **Figure 7**. The density ratio was calculated from the electrospun mat density divided by the solid rubber density. In case of carbon black loading, the density of the electrospun mats decreased as the carbon black loading increases. In case of different carbon black types at same loading, the density of the electrospun mats decreased with higher structure and surface area, but smaller particle size, while the density of the solid rubber was unaffected by the carbon black type. Density ratios can be used to compare the porosity of the fiber mats. A lower density ratio number indicates greater porosity of the membrane. Both density and density ratio of electrospun butyl rubber mats decreased with increasing carbon black loading, structure, surface area, and decreasing carbon black particle size. This is due to decrease in fiber diameter with increasing carbon black loading, structure, surface area, and decreasing carbon black particle size. These data can be used to help guide the selection of carbon black to tailor the mat properties for a specific application.

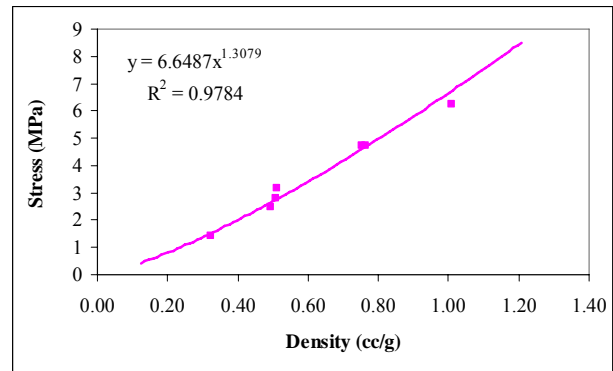
### 3.2 Mechanical Properties

The mechanical behavior of electrospun fiber mats depends on the fiber structure, such as the geometrical arrangement of the fibers (Hansen, 1993), properties of the carbon black filler, and interactions between the carbon black and butyl rubber. In addition, the density of the electrospun mat will play a role in the overall

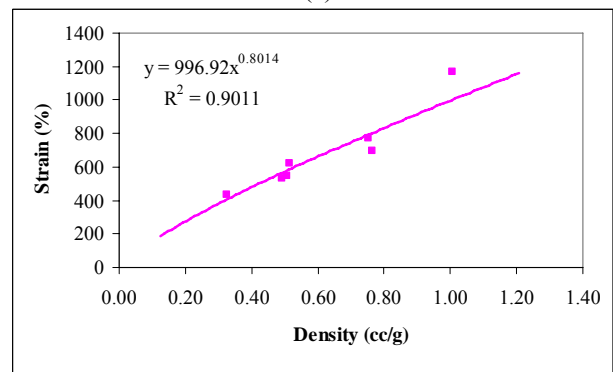
properties of the material. To illustrate this effect, **Figures 8a** and **8b** show characteristic plots of stress ( $\sigma_b$ ) and strain ( $\epsilon_b$ ) as a function of the density ( $\rho$ ), respectively, for several carbon black types in butyl rubber.



**Figure 7.** Effect of carbon black surface area on density at 25, 30 and 40 phr carbon black.



(a)



(b)

**Figure 8.** Effect of density on (a) stress and (b) elongation at break of electrospun butyl rubber mats with 30 phr carbon black.

The strong effect of the density of the electrospun butyl rubber on ultimate strength and elongation can be explained based on the theories of foams. Structural foams have a cellular structure and can be compared to

the pure polymer using relative densities. Because structural foams are generally not uniform in cell structure, they exhibit a considerable variation in properties with geometry, relations that can provide valuable guidance. For foams, both stress and strain at break show power law functions of density, according to Equations (4) and (5) (Klempner and Frisch, 1991).

$$\sigma_b(\rho) = k_{\sigma_p} \rho^A = 6.6487 \rho^{1.3079} \quad (4)$$

$$\varepsilon_b(\rho) = k_{\varepsilon_p} \rho^B = 996 \rho^{0.8014} \quad (5)$$

The electrospun butyl rubber mats also follow power law behavior with exponents of 1.30 and 0.80, respectively, for loadings of 30 phr carbon black. The value of the exponents A and B are dependent upon many parameters including carbon black loading.

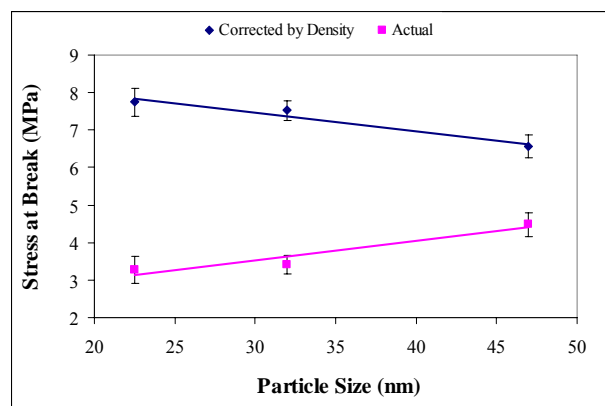
For electrospun mats one must also compensate for the change in density on the mechanical behavior. To compensate for the density differences, the density ratio was used to normalize these data to investigate the effect of particle size, surface area and structure of carbon black. Corrected values of these tensile properties were calculated by dividing the apparent data by the density ratio. The effect of carbon black particle size (related to surface area) on breaking strength, ultimate elongation, and 300% modulus of electrospun butyl rubber is shown in **Figures 9, 10, and 11**, respectively, for samples containing 25 phr carbon black. Surface area refers to the amount of carbon black surface available to interact with the elastomer. It is well known that the larger the surface area of particulate filler, the greater the interaction between the filler and rubber matrix. The surface area is inversely related to the size of the carbon black particles that fuse to form an aggregate. In general, smaller particle sizes of carbon black lead to increased tensile strength of solid rubber compounds.

As shown in **Figure 9**, when density differences were not considered, the electrospun butyl rubber shows the apparent breaking strength decrease as carbon black particle size decreases. This result can be explained by the reduction in density with decrease in particle size. When corrected for the density differences, decreasing particle size leads to the expected increase in tensile strength. These results are consistent with those of foam theory, where it was found that the tensile strength of latex rubber foam depends on its density. These results highlight the importance of density in determining the tensile strength of the electrospun fiber mats.

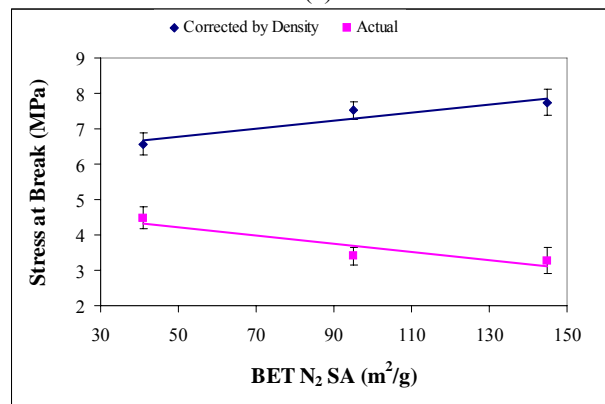
The dependence of elongation at break of electrospun butyl rubber on the particle size is shown in **Figure 10**. When uncorrected for the density, the elongation at break decreases with decreasing particle size. After correcting for density differences, the elongation at break shows the

expected increase in elongation with decreasing particle size.

As seen in **Figure 11**, smaller particle size led to decreased 300% tensile modulus when the values were uncorrected for density differences. When the values were corrected for density differences, the 300% tensile modulus increased with decreasing particle size. This result is consistent with behavior for solid rubber compounds, where smaller carbon black particle size results in a higher tensile modulus. Although the effects of carbon black on the rubber follow the behavior of solid rubber compounds, the influence on the mat properties must be considered in actual use. As a result, the influence of the carbon black on the rubber properties as well as the density must be determined.



(a)

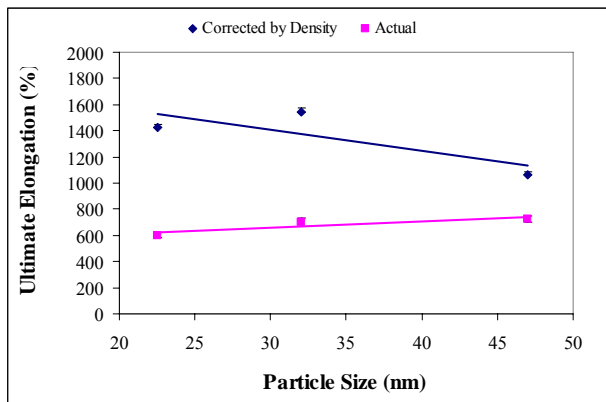


(b)

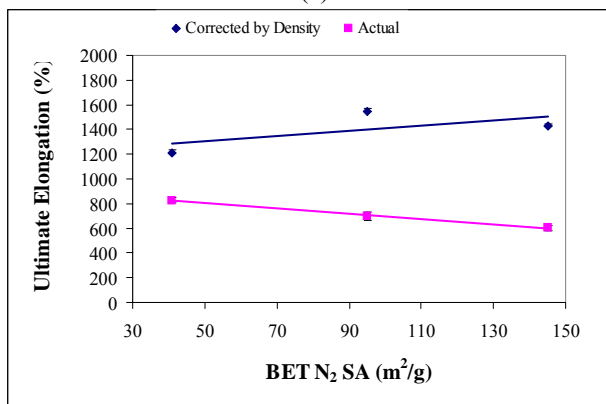
**Figure 9:** Effect of carbon black (a) particle size and (b) BET N<sub>2</sub> SA on breaking strength of electrospun butyl rubber mats.

In addition to the particle size, the structure of the carbon black will also influence rubber properties. As mentioned in the introduction, carbon black structure describes the number of particles strongly fused together to form an aggregate. When density differences were not considered, the apparent breaking strength decreased with increasing carbon black structure, but there was no significant change on elongation and 300% tensile

modulus of the electrospun butyl membranes. When corrected for the density difference, increasing carbon black structure leads to an increase in ultimate tensile strength, elongation and 300% modulus. In solid rubber compounds increasing carbon black structure leads to an increase in 300% modulus, while the effects on tensile strength are variable. In contrast to the corrected electrospun mats, in solid rubber compounds, increasing structure leads to decreasing elongation. Again, density plays a critical role in the properties of the electrospun butyl rubber membranes.



(a)



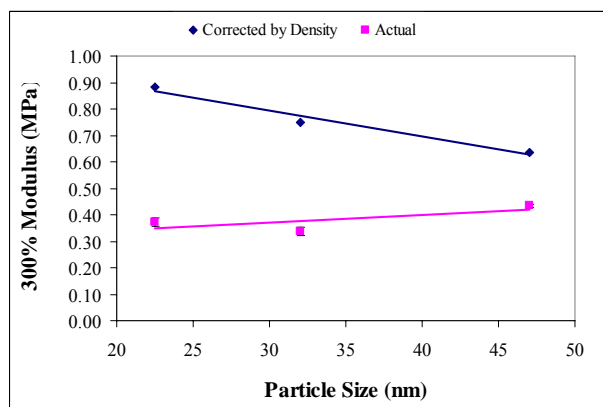
(b)

**Figure 10:** Effect of carbon black (a) particle size and (b) BET N<sub>2</sub> SA on elongation of electrospun butyl rubber mats.

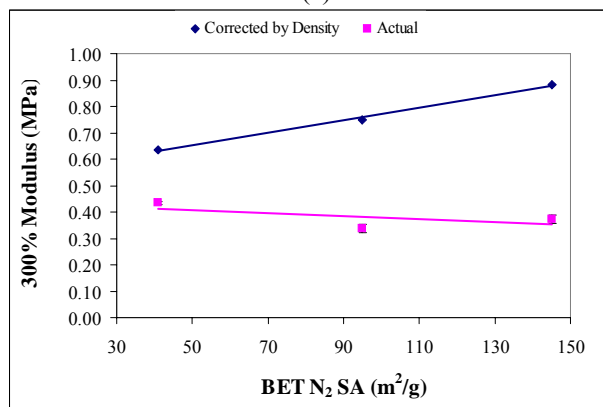
### CONCLUSIONS

The effect of carbon black type on the morphology and mechanical properties of electrospun butyl rubber nonwoven mats was investigated using carbon blacks with a range of particle sizes and structure. Fiber diameter decreased with decreasing particle size and increasing carbon black structure. Both electrical conductivity and solution concentration play an important role in determining the fiber formability and diameter. The effect of carbon black type in the butyl rubber compound on fiber morphology can also be seen in the density of electrospun mats. Density of the electrospun

mats decreased with smaller particle size and higher structure. The strong effect of the density of the electrospun butyl rubber on ultimate strength and elongation can be explained based on the theories of foams. Structural foams have a cellular structure and can be compared to the pure polymer using relative densities. For foams, both stress and strain at break show power law functions of density. The electrospun butyl rubber mats also follow power law behavior with exponents of 1.30 and 0.80, respectively for loadings of 30 phr carbon black. For electrospun mats one must also compensate for the change in density on the mechanical behavior. To compensate for the density differences, the density ratio was used to normalize these data to investigate the effect of particle size, surface area and structure of carbon black. After correcting for the difference in density, decreasing carbon black particle size and increasing structure caused an increase in stress at break, ultimate elongation, and modulus of the electrospun butyl membranes.



(a)



(b)

**Figure 11:** Effect of carbon black (a) particle size and (b) BET N<sub>2</sub> SA and on 300% modulus of electrospun butyl rubber mats.

### ACKNOWLEDGEMENTS

The authors would like to acknowledge Cabot Corporation and R. T. Vanderbilt for materials. Some of the authors would like to acknowledge the financial

support of the U.S. Army Natick Soldier Center. The authors would also like to recognize the technical contribution of Dr. Jun Lee in providing SEM images.

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