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Abstract

Rubber material generally behaves as an electrical insulator, and vapor grown carbon fiber (VGCF) has excellent electrical conductivity. In our study, we mixed carbon nanofiber (VGCF) into styrene–butadiene rubber and investigated the relationship between strain and the electric capacitance of vulcanized rubber filled with VGCF, of which the hardness was not changed. The electric capacitance of the rubber filled with VGCF increased with VGCF content but decreased with increasing tensile strain. We confirmed that the change rate of electric capacitance is related to the VGCF content of the fillers. In order to investigate the relationship between strain and electric capacitance of rubber with VGCF, it is feasible to apply rubber composites filled with VGCF as a strain sensor.

Keywords

Electric capacitance, electrical volume resistivity, carbon nanofiber, rubber, strain, hardness, measurement, electrodes

1. Introduction

A nanofiber, represented by carbon fiber synthesized by the vapor phase method (Vapor Grown Carbon Fiber or VGCF), has a high-aspect ratio with a diameter of scores of nanometers, excellent mechanical characteristics and electrical properties, and a lower price than carbon nanotubes; therefore, it is applied in various fields. For example, many studies have used VGCF as reinforcement filler and electrically conductive filler for plastics [1–13]. Materials filled with electrically conductive fillers are used for electrodes.

Vulcanized rubber is an electrical insulator that allows much deformation; thus, it is used in many industrial products. When rubber is filled with electrically con-

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ductive filler, it becomes electrically conductive rubber [14]. The minimum volume of filling (threshold value) for providing electrical conductivity varies, depending on the form of electrically conductive filler. When spherical carbon black (CB) is used, not only is a large volume of filling required, but also rubber abruptly enters an insulating state when a large strain is applied.

Therefore, we focused on VGCF, which is made of the same material as CB but takes the form of fiber, and found that rubber filled with VGCF instead of CB has improved tear strength, which is an important feature for rubber material, while maintaining the original hardness of rubber [15]. Furthermore, we found that rubber filled with VGCF has more stable electrical characteristics than that filled with CB, and the minimum volume of filling to provide electrical conductivity (threshold value) is improved. The electrical resistance of rubber material increases under strain; therefore, using such a relationship and newly developed electrodes, we found that such rubber material can be applied as high-strain sensors [16]. However, some studies indicate that it takes a considerably longer time for the measurement of electrical resistance to become stable and that the values of electrical resistance are high. Todoroki and co-workers [17] investigated electrical resistance under strain (3%) in the composite material of VGCF and flexible epoxy resin, and calculated the electrical conductivity of the material filled with carbon fiber from the theory of percolation as well as the tunnel effect. Dharap *et al.* [18] filled PVA with nanotubes and tried to apply PVA film as a strain sensor (for strains of 1% or less) by utilizing the relationships between strain and electrical resistance.

In this study, rubber filled with VGCF is replaced with an equivalent circuit containing parallel connections of an electrical resistor and a capacitor (Fig. 1). The relationship between the volume of VGCF filling and electric capacitance and that between strain and electric capacitance in rubber are examined to examine the possibility of applying it to strain sensors that utilize electric capacitance changes and allow much deformation.

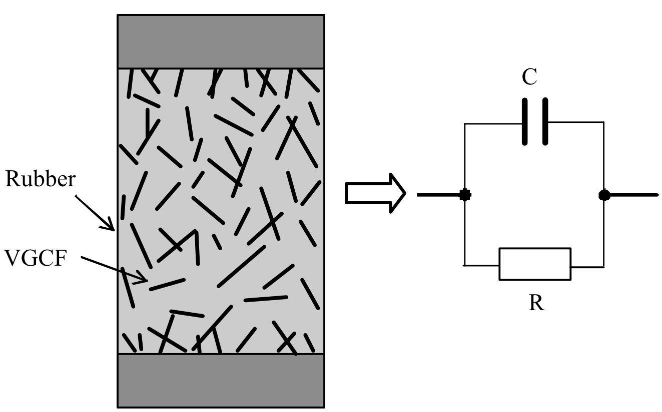

Figure 1. Equivalent circuit of VGCF-filled rubber.

2. Test Apparatus and Samples

2.1. Samples

Samples with the compositions listed in Table 1 were prepared to investigate the electric capacitance of rubber filled with VGCF. For the matrix, styrene–butadiene rubber (SBR, made by Japan Zeon Co. Ltd.), which is mainly used for automobile tires, was used. VGCF (Showa Denko Co. Ltd.) and CB (N660, Tokai Carbon Co. Ltd.) were used as reinforcement fillers for that material. VGCF has an average diameter of 150 nm, an average length of 15 μm, and a true density of 2 g/cm^3.

Sample 1 is filled with VGCF alone, Sample 2 is filled with CB alone, and Sample 4 is filled with a mixture of VGCF and CB at a ratio of 1:1. Sample 3 was prepared by filling with CB and VGCF so that their total volume was kept constant (CB + VGCF = 60 PHR) by considering the past study result that the hardness of rubber is constant within this range [15], to investigate electric capacitance changes while the volume of VGCF changes. In Samples 2–4, the components other than

Table 1.
Composition of compounds used by weight (PHR)

	Composition	1	2	3	4	5	6	7
Sample 1	SBR1502	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	VGCF		10.0	20.0	30.0	40.0	50.0	60.0
	ZnO	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	6PPD	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Process oil	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Sulfur	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	TBBS	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Total	113.0	123.0	133.0	143.0	153.0	163.0	173.0
Sample 2	SBR1502	100.0	100.0	100.0	100.0			
	N660	50.0	60.0	70.0	80.0			
	Total	163.0	173.0	183.0	193.0			
Sample 3	SBR1502	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	N660	60.0	50.0	40.0	30.0	20.0	10.0	
	VGCF		10.0	20.0	30.0	40.0	50.0	60.0
	Total	173.0	173.0	173.0	173.0	173.0	173.0	173.0
Sample 4	SBR1502	100.0	100.0	100.0	100.0	100.0		
	N660		10.0	20.0	30.0	40.0		
	VGCF		10.0	20.0	30.0	40.0		
	Total	113.0	133.0	153.0	173.0	193.0		

SBR1502: Zeon Co. Ltd. Bound styrene 23.5 wt%.
6PPD: N-1,3-Dimethylbutyl-N′-phenyl-paraphenylene-diamine.
TBBS: N-*tert*-butyl-2-benzothiazyl sulfeneamide.
N660 Carbon black: Tokai Carbon Co. Ltd.

SBR1502, VGCF and N660 and their mixture ratios are the same as in Sample 1; therefore, their description is omitted here.

To eliminate the influence of the rubber production process, all samples in Table 1 are prepared by the following procedure. According to the composition table, components other than sulfur and N-*tert*-butyl-2-benzothiazyl sulfeneamide (TBBS) (e.g., styrene–butadiene rubber, CB and VGCF) are roughly kneaded for 5 min in a Bunbury mixer. They are then kneaded together with sulfur and TBBS for 10 min, using an open roll mill, and the mixed rubber is put into a 2 mm-deep mold, vulcanized with a hot press for 30 min at 160°C and then molded.

2.2. *Measuring Instrument and Specimens*

In the measurement of electric capacitance, it is possible to measure electric resistance and capacitance while applying strain, and the specimen has a large contact resistance. Therefore, the circuit of a four-terminal system (Fig. 2) is used so that stable measurement can be achieved by avoiding such an influence; current is applied to two terminals outside the specimen, and the potential difference is measured on the two terminals installed inside the specimen. Rectangular specimens (complying with JIS K 6251-1993) are used in both the grain and anti-grain directions of rubber. Each specimen is 50 × 10 × 2 mm, with 3 mm electrodes, a distance of 6 mm between the electrodes and 10 mm-long chucks at both ends. Electrodes are installed on the surface of the specimen with platinum deposition, and a copper wire is bonded on it using flexible conductive bond (Conductive Epoxy CW2400, Circuit-works Co. Ltd.).

For easy application in the future, a low-cost 3511-50 LCR High-tester (HIOKI Co. Ltd.) will be used to measure the electric capacitance, where the measurement signal level is set to 1 V rms and the measurement frequency to 1 kHz. The specimen is pulled by a tension tester (Shimazu Seisakusho, Autograph, AG20kN), and strain in the specimen is measured by taking photographs at each volume of move-

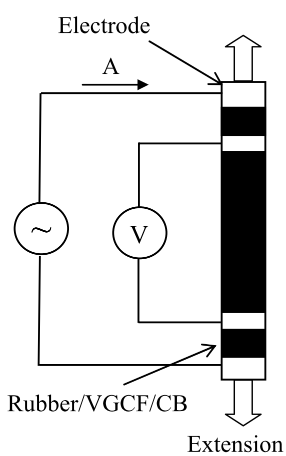

Figure 2. Electric circuit and electrode.

ment using a digital camera and obtaining the distance between the terminals for measuring the potential difference using image analysis software. The pulling speed is 3 mm/min, and testing temperature is 25°C. Five tests are conducted on each specimen, and the results are averaged.

3. Test Results and Discussion

3.1. Relationship between Electric Capacitance and VGCF Filling Ratio

The electric capacitances of each specimen with no strain in the grain and anti-grain directions were measured using the method depicted in Fig. 2. Compared with the measurement of electric resistance, the measurement became stable within a relatively short time (several seconds). The relationship between the average of electrical capacitances of the specimens measured and the volume of VGCF filling is plotted in Fig. 3.

As depicted in the figure, electric capacitance increased as the volume of VGCF filling increased. The electric capacitances in Sample 1 (SBR rubber alone) and Sample 2 (filled with CB alone) were too small to measure within the measurement range of this instrument. However, when the volume of VGCF filling is represented on the horizontal axis, each specimen has similar values of electric capacitance, regardless of whether it is filled with CB or not. In other words, no improvement in electric capacitance in pace with the increase in the volume of CB filling was confirmed. Electric capacitance increased at a higher rate in specimens that were filled with larger volumes of VGCF.

SBR rubber is an insulator; however, when it is filled with VGCF, which has high-electric conductivity and a high-aspect ratio, a conductive network is formed in part of the specimen and the conductive network composed of VGCF near the electrodes in particular expands the area of the electrodes. Furthermore, the equivalent distance between the electrodes is shortened by the conductive network formed,

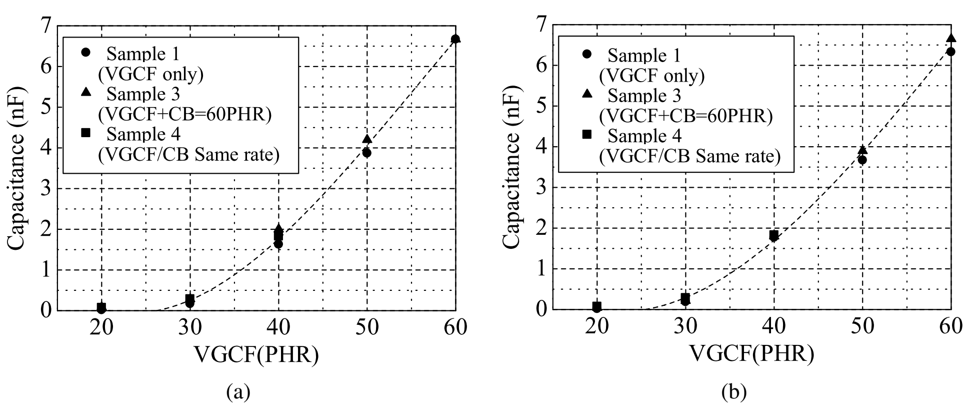

Figure 3. Capacitance of rubber filled with VGCF and CB (longitudinal). (a) Longitudinal and (b) transverse.

and these are considered to be the cause of higher electric capacitance in rubber filled with VGCF than that in rubber alone. CB is almost spherical, and it is far more difficult to form a conductive network by filling with a small volume of CB than with VGCF. It is conjectured that this is why no effect of CB in improving electric capacitance was confirmed in this measurement.

The measured values in the grain direction and anti-grain direction were almost equal in each specimen, as indicated in Fig. 3(b); therefore, no effect of the difference in grain direction was observed within the measurement range of this instrument.

3.2. Relationships between Strain and Electric Capacitance in Specimens

To investigate the relationships between strain and electric capacitance in specimens, the electric capacitance in rubber samples prepared by filling with VGCF are measured while pulling them with a tensile tester.

Figure 4(a) depicts the measured values of the relationships between strain and electric capacitance in specimens in the grain direction of Sample 1. The horizontal axis represents the strain obtained by taking photographss of the space between the electrodes of the specimen using a digital camera, and the vertical axis represents the average of measured values of electric capacitance. In the specimens filled with VGCF in volumes of 10 PHR and 0 PHR, the values were too small to measure with this LCR measuring instrument. Electric capacitance decreases as strain increases (Fig. 4), and changes within the range of 100% are steady. It is necessary to consider the influence of static electricity, and a high-level ohmmeter is required for measuring electric resistance [15] because rubber material itself has considerably high resistance; however, measurement of electric capacitance involves good stability and reproducibility of data and can be achieved with a low-price LCR measuring instrument. Thus, we conclude that it is advantageous for future applications.

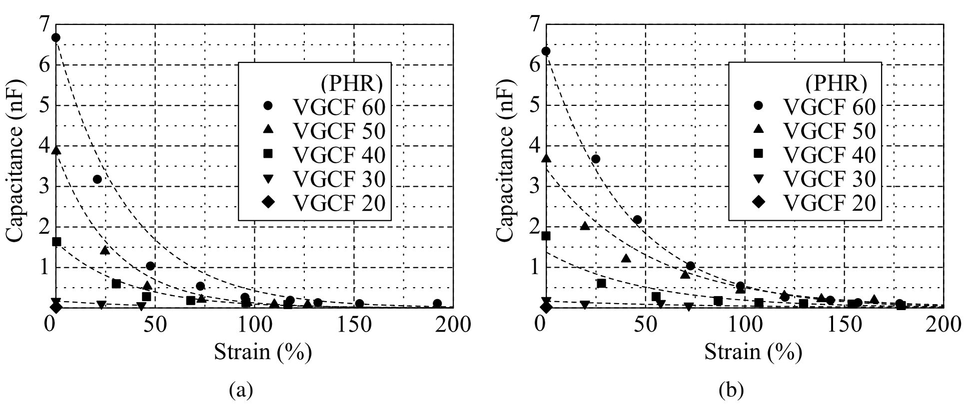

Figure 4. Relationship between strain and capacitance of Sample 1. (Changes in VGCF content, CB 0). (a) Longitudinal and (b) transverse.

Figure 4(b) depicts the measurements of the relationship between the strain and electric capacitance in specimens in the anti-grain direction of Sample 1. The measured values in the anti-grain direction of rubber are almost equal to those in the grain direction. The same results were also obtained in Samples 3 and 4, indicating that the electric capacitance in rubber filled with VGCF is not affected by either the grain or anti-grain direction, unlike mechanical characteristics.

In Sample 2, which is filled with CB alone, the electric capacitance is too small to measure with this instrument.

Figure 5 depicts the measured values of the relationship between strain and electric capacitance in the grain direction of Sample 3. In Sample 3, the volume of VGCF filling is changed, while the sum of the volumes of VGCF filling and CB filling (i.e., 60 PHR) is kept constant, since an important mechanical characteristic of rubber material is that hardness is kept constant when the total volume of fillers is kept constant [15]. This sample demonstrates the same behavior as that of Sample 1, where electric capacitance decreases as strain increases, as depicted in Fig. 5.

Figure 6 plots the relationship between the strain and electric capacitance in the specimen in the grain direction of Sample 4. Also in Sample 4, it can be seen that electric capacitance decreases as strain increases.

The elastic modulus of SBR rubber is only several MPa, while that of VGCF is several TPa [1]; therefore, when rubber filled with VGCF is extended by pulling, VGCF is scarcely extended, whereas rubber is extended by a large amount. In other words, the relative distance between VGCFs increases in rubber filled with fillers. This fact was also confirmed through observation with a laser microscope in a previous report [16]. It is conjectured that this is because the conductive network composed of VGCF was destroyed; the area of electrodes decreased and electric capacitance decreased, due to the extension of rubber filled with fillers.

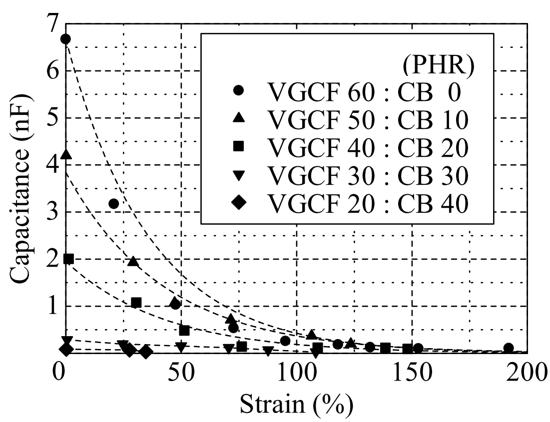

Figure 5. Relationship between strain and capacitance in longitudinal direction in Sample 3 (VGCF + CB = 60 PHR).

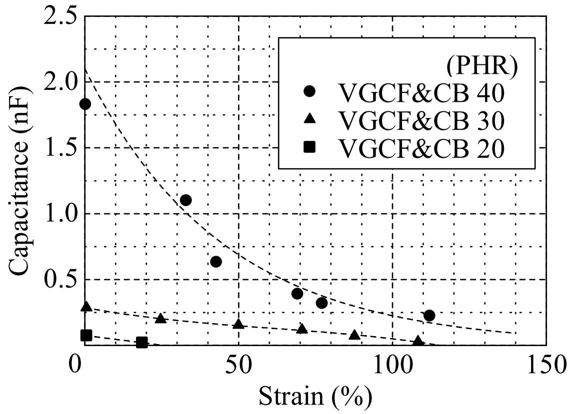

Figure 6. Relationship between strain and capacitance of longitudinal in Sample 4 (Content: VGCF = CB).

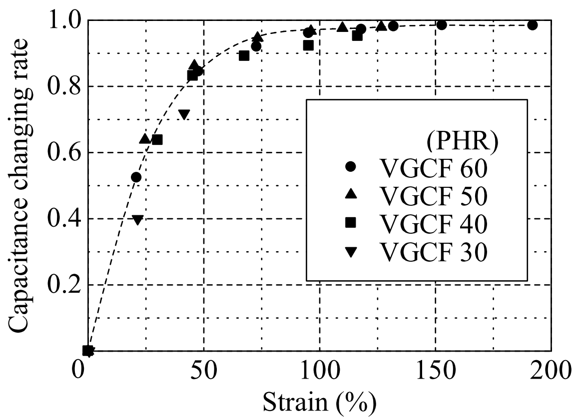

Figure 7. Relationship between strain and capacitance changing rate of longitudinal direction in Sample 1.

3.3. Strain and Capacitance Change Rate

When the electric capacitance at no strain in the specimen ($\varepsilon = 0$) is denoted as C_0 and the electric capacitance at a certain strain is denoted as C_n, the capacitance change rate can be expressed as

$$\text{Capacitance change rate} = \frac{C_0 - C_n}{C_0} = \frac{\Delta C}{C_0}. \quad (1)$$

Figure 7 depicts the capacitance changing rates in the grain direction of Sample 1, as obtained from equation (1) and Fig. 4. The horizontal axis represents the strain in the specimen. Almost the same curves are drawn for Sample 1, regardless of the volume of VGCF filling. Specimens filled with much VGCF have larger ranges to cover the strain. While capacitance changing rates of the specimen up to 200% of

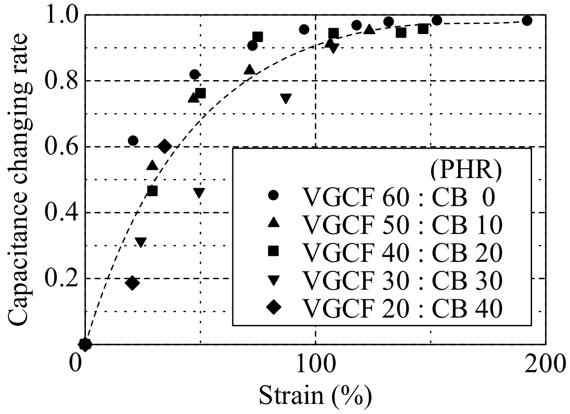

Figure 8. Relationship between strain and capacitance changing rate of longitudinal direction in Sample 3.

strain have been confirmed, changes are intense within the range of 100% strain; thus, this range is suitable for strain sensors.

Figure 8 depicts the capacitance changing rates in the grain direction of Sample 3. Although dispersion of data is larger than in Sample 1 due to filling with CB, roughly the same curves are depicted. The capacitance changing rate in specimens changes intensely within the range of 100% strain, as in Sample 1; therefore, it is suitable for use as a strain sensor.

From the above results, it can be seen that filling with CB scarcely forms a conductive network, so the volume of VGCF filling is the main factor that mainly affects the capacitance changing rate.

4. Relationship between Electric Capacitance under Strain and the Volume of VGCF Filling

4.1. Changes in Electric Capacitance Depending on the Distance between Electrodes

When electrodes are attached to a dielectric material, the electric capacitance can be expressed as

$$C = \varepsilon_{\mathrm{r}}\varepsilon_0 \frac{S}{d}, \tag{2}$$

where ε_0 is the dielectric constant of vacuum ($\varepsilon_0 = 8.854 \times 10^{-12}$ F/m), ε_{r} is the dielectric constant of the material, S is the area of electrodes, and d is the distance between electrodes. When rubber filled with VGCF is pulled (Fig. 2), the distance (d) between electrodes increases as the material is extended, leading to a decrease in electric capacitance.

The dielectric constants of rubber filled with each volume of VGCF were obtained from equation (2), using the electric capacitance in each sample with no

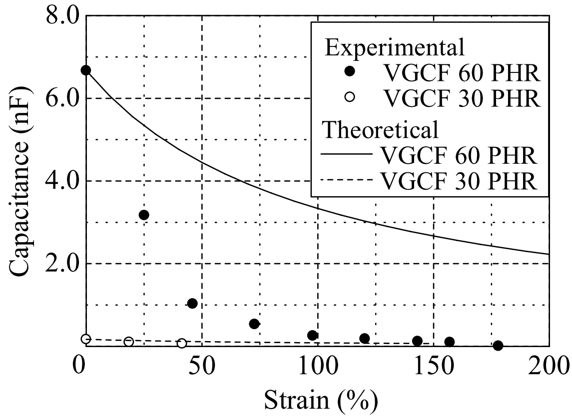

Figure 9. Comparison of the experiment data with the theoretical data. (The distances of electrodes are changed.)

strain (Fig. 3). The dielectric constant obtained was substituted in equation (2), the electric capacitance with some strain was calculated, and the result was compared with the experiment result (Fig. 9). In Fig. 9, the black circles represent experimental results for Samples 1–7, and the white circles represent those for Samples 1–4; the solid line and the dotted line represent calculated values.

Although the difference in experimental values is small in samples with a small volume of VGCF filling (30 PHR), the calculated value deviates from the experiment value as the volume of VGCF filling increases. Samples filled with CB also indicate the same results as the samples with a smaller volume of VGCF filling. SBR rubber with a considerably small dielectric constant and a small volume of VGCF filling can be expressed by equation (2) in the same manner as for ordinary dielectric materials. However, the electric capacitances of samples with no strain increase due to filling with VGCF and electric capacitance changing rate due to extension change greatly. Therefore, we conclude that some influences other than that of the distance between electrodes exist.

4.2. Changes in Electric Capacitance due to Changes in the Apparent Area of Electrodes

VGCF has high-electric conductivity; therefore, when rubber is filled with VGCF, it can be assumed that VGCF contacting electrodes (near the electrodes in Fig. 1) function as electrodes, resulting in a larger area of electrodes. Thus, the electric capacitance in rubber filled with VGCF is higher than that in rubber alone. To discriminate the area increased by VGCF from the original area of electrodes, the former is defined here as the apparent area of electrodes. The content of VGCF near the electrode becomes higher as the volume of VGCF filling increases; thus, the effect of increasing the apparent area increases, and the electric capacitance becomes larger as the specimen contains a larger volume of VGCF filling.

Here, when the apparent area of electrodes, which increases when VGCFs contact the electrode, is denoted as ΔS, electric capacitance can be expressed by

$$C = \varepsilon_r \varepsilon_0 \frac{S + \Delta S}{d}, \tag{3}$$

where ε_r is the dielectric constant of SBR rubber, which is 2. We calculate the volume of VGCF contained in rubber filled with VGCF from the specific gravities of rubber and VGCF using Table 1, and substitute the electric capacitance in the grain direction in Fig. 3 into the equation. The relationship between the volume content of VGCF and the apparent area of electrodes can then be obtained.

It was demonstrated in Section 4.1 that the distance between electrodes, d, increases when strain is applied to the sample, leading to lower electric capacitance. However, another factor that can be considered is that the apparent area of electrodes decreases when some VGCF separates from the electrodes due to the far higher elastic modulus of VGCF than rubber and, thus, the value of electric capacitance decreases. In other words, electric capacitance decreased because the volume of VGCF in a unit length in the direction of extension decreased, the number of VGCFs contacting the electrode decreased, and the number of VGCF networks as conducting paths decreased.

However, the distance between VGCFs becomes shorter because the sectional area of the sample decreases in the direction (y) that is perpendicular to the extension (x) due to the Poisson effect, and therefore, the number of conductive networks near the electrodes increases. To investigate the degree of this effect, a compressive load was applied in the y direction, which is perpendicular to the extension, using a tension tester (Fig. 10), and the relationship between the strain in the y direction and the electric capacitance under such a load was determined. Figure 11 depicts an example of such measurement, where electric capacitance improves slightly as the strain in the y direction increases. However, it was found that this effect is smaller than that in the x direction.

Using the relationship between the volume content of VGCF and the apparent area of electrodes, as identified in Fig. 3 as well as equation (3), changes in electric capacitance under strain in rubber filled with VGCF were obtained. An example of the predicted results obtained without considering the effects of extension or strain in the direction perpendicular to the extension is depicted in Fig. 12. Samples 1–7

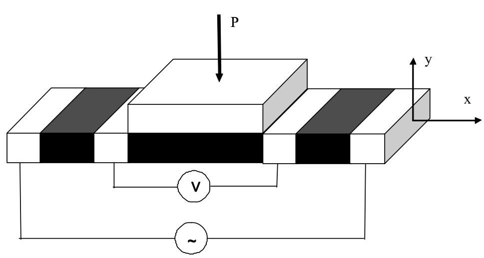

Figure 10. Method of measuring capacitance of VGCF/rubber with y-direction strain.

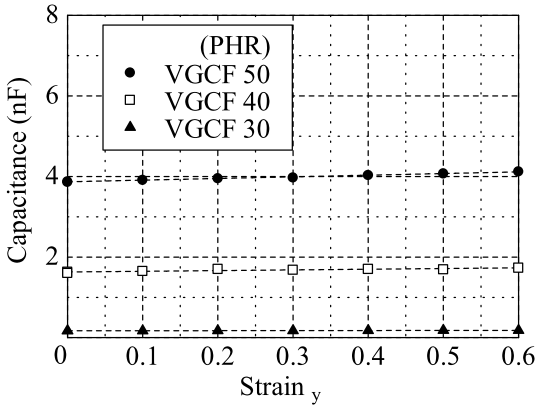

Figure 11. Relationship between strain applied in the *y*-direction and longitudinal capacitance in Sample 1.

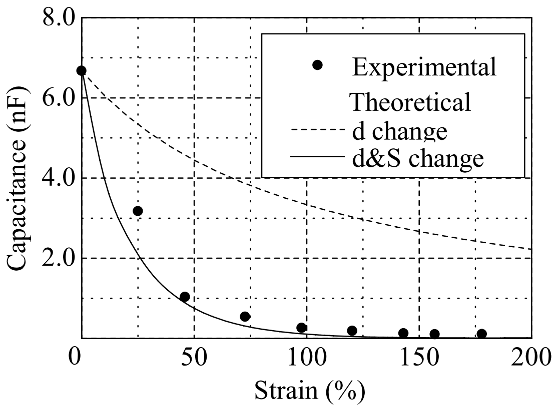

Figure 12. Comparison of the experiment data with the theoretical data. (The distance and area of electrodes are changed.) (Samples 1–7.)

(VGCF 60 PHR) are used. The black circles represent experiment values, and the solid line represents the calculation result considering the increase in the equivalent area of electrodes caused by the proposed volume of VGCF filling, indicating the calculation values that approximate the actual measurement values. In other words, it can be seen that the apparent area of electrodes largely affects the electric capacitance of rubber material filled with VGCF because calculation values are roughly equal in all samples, including those filled with a large volume of VGCF, a small volume of VGCF, and a mixture of VGCF and CB, confirming the validity of the proposed calculation method.

5. Conclusion

To investigate the electric capacitance characteristics and changes in electric capacitance under strain of rubber filled with nanofiber, we prepared SBR rubber samples filled with VGCF alone, filled with CB alone, and filled with a mixture of VGCF and CB, using an ordinary rubber manufacturing method, and measured the electric capacitance of each of them using the four-terminal method. Furthermore, we measured the changes in electric capacitance with tensile strain applied to those samples.

The electric capacitance of rubber filled with VGCF increases as the volume of VGCF filling increases, where the electric capacitance is determined by the volume of VGCF filling, regardless of whether the rubber is filled with CB or not. Furthermore, the electric capacitance of rubber filled with VGCF decreases as the strain in the specimen increases. Changes in capacitance are remarkable under 100% or less strain.

A possible reason for improved electric capacitance in rubber filled with VGCF may be that filling with conductive VGCF causes formation of a conductive network near the electrodes, and the apparent area of the electrodes increases. When the specimen is extended, however, VGCFs are considered to separate from electrodes, causing a smaller apparent area of electrodes and significantly reducing electric capacitance.

From the above results, application of such rubber to high-strain sensors that utilize electric capacitance can be considered feasible.

Acknowledgements

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