Actuator Membrane Comprising Natural Rubber Filled with Activated Carbon

Darika Jaaoh[*]

Physics Program, Faculty of Science Technology and Agriculture, Yala Rajabhat University,
Yala 95000, Thailand

Natural rubber (NR) is an electrostrictive polymer that responds to electrical fields. The permittivity of NR may be increased by doping it with conductive particles. In this study, activated carbon was employed to increase the amounts of free space and interphase charges between a rubber and a filler. Activated carbon was combined in the rubber phase in ratios of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 parts per hundred rubber (phr). The morphology of NR membranes with activated carbon was investigated. In addition, their mechanical, electrical, and electrical response properties were assessed. A proposed preparation method was compared with the conventional preparation method. The results demonstrated that the activated carbon particles blended into NR by the proposed preparation method were distributed homogeneously. When the amount of activated carbon was increased, the dielectric constant increased, but the modulus decreased. The maximum electrostriction coefficient (M_{33}) of the NR membrane with 3.0 phr activated carbon prepared by the proposed preparation method was 3.51×10^{-15} m^2/V^2. This value was greater than that obtained by the conventional preparation method and close to that of polyurethane, a synthetic polymer material commonly used in actuators.

1. Introduction

Electroactive materials change their form when an external electric field is applied. Electroactive polymers (EAPs) are used in actuators, sensors, and transducers. An actuator is a device that expands and contracts when it is subjected to an electric field. Generally, ceramics are used to induce the electrical response, such as a piezoelectric ceramic generator. However, ceramics are limited in terms of their weight, flexibility, and shape sophistication. Lightweight polymeric materials with high flexibility have been considered as an alternative to orderly structured ceramics for electromechanical applications.[1] Natural rubber (NR) is a highly flexible polymer;[2] when a force applied to NR is removed, NR immediately returns to its original shape. However, it also has a low electrical response.[3] To overcome this problem, several attempts aim to develop electroactive NR membranes with high electrical conductivity, and different compound preparation methods have been proposed.

Activated carbon is generally produced from different organic precursors, such as biomass, coal, polymers, and natural or synthetic fibers, subjected to carbonization and activation processes. Its properties include high conductivity, large specific surface area, chemical stability, and low cost.[4] Hence, in this study, the electrostriction behaviors of NR and NR composites with various contents of activated carbon were investigated.

2. Literature Review

This article focuses on the electrostriction phenomena of NR filled with an activated carbon membrane as a function of filler concentration and the effects of the compound preparation method and external electric field strength on the response of the actuator. Theoretically and experimentally, they are proposed on the basis of electrostriction behavior.

2.1 Electrostriction mechanism

Electrostriction occurs in all dielectric materials regardless of their polarity. This effect causes the reorientation of random dipoles in the material under an applied electric field and leads to material actuation.[5] The operation of polymers can be represented by a parallel plate capacitor. Here, we consider an electrostrictive polymer sandwiched between two electrodes in the first and second directions (just as a vector in a three-dimensional space), with an electrical field applied along the thickness direction (third direction), and the electric-field-induced strain is measured in the third direction. The electrostriction coefficient (M) can be expressed as

$$M \propto \varepsilon_0 \left(\varepsilon_r - 1 \right)^2 / \varepsilon_r Y, \tag{1}$$

where ε_r is the dielectric constant, ε_0 is the dielectric permittivity of vacuum (8.854×10^{-12} F/m), and Y is Young's modulus (inverse of the elastic compliance, $1/s$).

Equation (1) corresponds to an equation reported by Guillot and Balizer,[6] who suggested that M is proportional to $\varepsilon_0(\varepsilon_r - 1)^2/\varepsilon_r Y$ for EAPs. Thus, the electric-field-induced strain in the longitudinal direction, S_3, can be written as

$$S_3 = -M_{33} E_3{}^2, \tag{2}$$

where the negative sign indicates the contraction of the electrostrictive polymer in the thickness direction.

2.2 Electrostatic effect

In addition to the electrostriction effect, the response strain is also quadratically related to the applied electric field according to the Maxwell stress effect (electrostatic force). The Maxwell stress is related to the Coulomb interaction between charges on electrodes, which induces the

electric field required for the contraction of the material. This force induces the actuation mechanism in soft elastomers such as acrylic and silicone rubber.

For an isotropic solid without mechanical constraints, the Maxwell strain in the thickness direction (S_M) can be written as

$$S_M = -\left(\varepsilon_0 \varepsilon_r E_3^2 / 2Y\right) = M_M E_3^{\,2}, \tag{3}$$

where M_M is the apparent electrostriction coefficient determined by the contribution of the Maxwell stress. The Maxwell stress is caused by the electrostatic force between the electrodes, force between the electrodes and this causes the film to deform in the plane perpendicular to the applied field and stress.

In the experiment of actuation, the apparent strain (total strain, S) is a combination of the strain from the electrostriction effect (S_E) and the strain from the Maxwell stress effect (S_M), and can be written as

$$S = S_E + S_M = ME^2, \tag{4}$$

where M is the apparent electrostriction coefficient.

3.   Materials and Methods

In this study, we prepared NR filled with activated carbon and carried out experiments to determine the morphology, mechanical characteristics, electrical properties, and electrostriction behavior of NR/activated carbon membranes.

3.1   Materials

The matrix material was latex with a high ammonia concentration (HA, 60 wt% solid content). The chemicals used for rubber vulcanization, supplied by Boss Optical Limited Partnership (Songkhla, Thailand), were 10% potassium oleate, 10% potassium hydroxide, 50% sulfur, 50% zinc dibutyl dithiocarbamate (ZBDC), 50% Lowinox CPL, and 50% zinc oxide (ZnO). Activated carbon (product number 902470), which was supplied by Sigma-Aldrich Pte Ltd. (Singapore), was combined in the rubber phase in ratios of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 phr.

3.2   Preparation of NR-filled activated carbon

In the conventional preparation method, NR latex in a beaker was smoothly stirred by a three-blade propeller stirrer at 120 rpm. Then, 10% potassium hydroxide and 10% potassium oleate solutions were added, along with a vulcanizing agent, an accelerator, and an activator to disperse the ingredients. Also, 50% Lowinox CPL was added as an emulsifier. Finally, various contents of activated carbon were dispersed in distilled water using a high-frequency sonicator (≈ 40 kHz) for 25 min, then added to the mixture. In the proposed method, polyoxyethylene(23)

lauryl ether (known as Brij-35) was added dropwise to the NR/activated carbon compound. Then, the mixture was left to stand for about 24 h to evacuate bubbles. NR/activated carbon composite membranes were formed by casting. Then, the composite membranes were dried at room temperature for about 20 min, then vulcanized at 120 °C for 15 min.

3.3   Testing and characterization

The morphology of the composite membranes was determined by scanning electron microscopy (SEM). Their mechanical characteristics were evaluated using a universal testing machine. The electrical properties were measured as a function of filler concentration at a low frequency (20 Hz) using an LCR meter (HAMEG, HM8110). The electrostriction behavior of the NR/activated carbon membranes was investigated at a low electric field ($E < 3$ MV/m) by measuring the strain-induced electric field with a photonic displacement sensor. All composite samples were obtained as films with a thickness of approximately 100 ± 10 μm; they were mounted on a brass electrode and subjected to a slowly increasing excitation voltage with the assistance of a high-voltage lock-in amplifier (Trek 610E) at a sufficiently high electric field.

4.   Results and Discussion

4.1   Morphology

The shape and size distributions of the dispersed phase, as well as particle dispersion, were assessed by SEM. The effects of preparation methods on the morphologies of polymer composite films were investigated. According to the cross-sectional SEM images of the NR/activated carbon composites shown in Fig. 1, the agglomeration of filler particles tended to increase with the activated carbon content. The composite membranes obtained by the proposed preparation method exhibited good phase dispersion within the matrix, and excessive agglomeration was avoided by using Brij. This might be due to the interaction between the NR matrix and the activated carbon filler. The excessive addition of Brij surfactants to the system will decrease the surface tension of the latex suspension. Moreover, this preparation method appears to be advantageous for the fabrication of composite membranes.

4.2   Mechanical and electrical properties

To determine the effect of activated carbon in the NR phase on the response of the actuator, we also monitored the Young's modulus of all specimens. Each sample was evaluated using a universal testing machine. The composites were stretched at a strain rate of 500 mm.min^{-1}. The elongation was plotted against the response force, then the Young's modulus of each composite was analyzed.

Figure 2(a) shows the variation of Young's modulus with the activated carbon weight fraction. The modulus slightly increases with the carbon weight fraction at a low filler concentration (<1.5 phr). The effect of filler loading on Young's modulus is mainly due to the increased interfacial
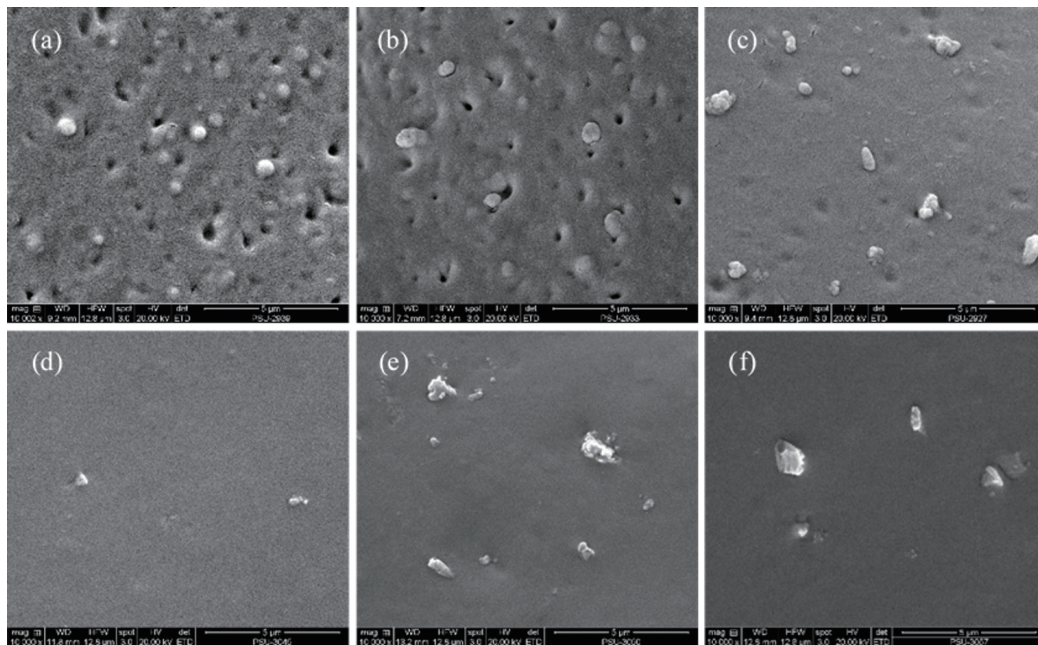
Fig. 1.   (Color online) SEM images of NR/activated carbon with (a, d) 1.0 part per hundred rubber (phr), (b, e) 2.0 phr, and (c, f) 3.0 phr activated carbon obtained by conventional preparation method (a–c) and proposed preparation method (d–f).
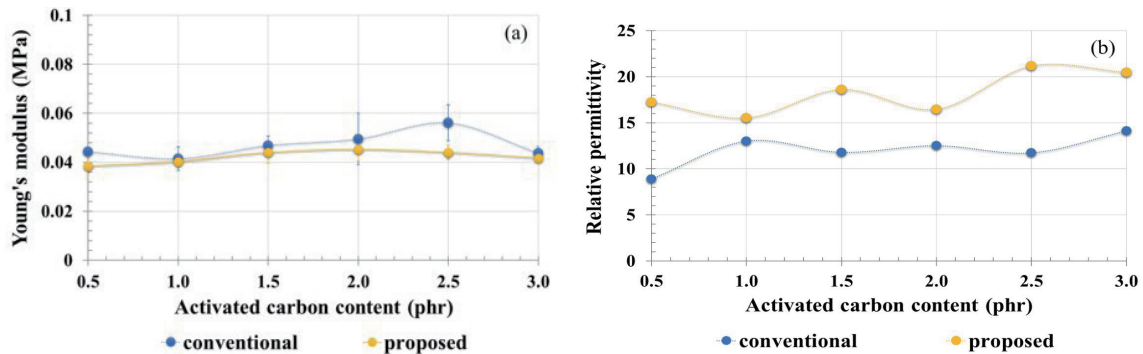

Fig. 2.   (Color online) Mechanical and electrical properties of NR/activated carbon membrane: (a) Young's modulus and (b) relative permittivity as functions of filler content.

surface area between filler particles and the host matrix.[7] Thus, Young's modulus tends to be constant at a higher content of activated carbon in the dominant matrix. However, the modulus of the membranes is slightly higher with the conventional preparation method than with the proposed preparation method. The results may be attributed to the residue of Brij in the composite.

Relative permittivity as a function of filler content for the two preparation methods is shown in Fig. 2(b). The relative permittivity increased with the activated carbon content. This is attributed to the Maxwell–Wagner interfacial polarization between the activated carbon filler

and the NR matrix, which often occurs in heterogeneous composite materials and results from orientation polarization reducing the number of polar functional groups in polymer chains.[8] The membranes obtained by the proposed preparation method showed a higher permittivity than those obtained by the conventional preparation method owing to the easy and effective movement of molecular chains in a pulsed electric field.

4.3 Electrostriction behavior

At 20 Hz, the strain in the direction of the electric field was measured to maximize the strain response. The longitudinal strain of all composites had a quadratic relationship with the electric field regardless of the preparation method used. However, above an electric field of 3 MV/m, the strain became saturated. Figures 3(a) and 3(b) show the strain responses plotted against the square of the applied electric field for the composites prepared by the conventional and proposed preparation methods, respectively. The longitudinal strain of all samples showed a linear response that followed Eq. (2). Figure 4 shows the electrostriction coefficients of the composite
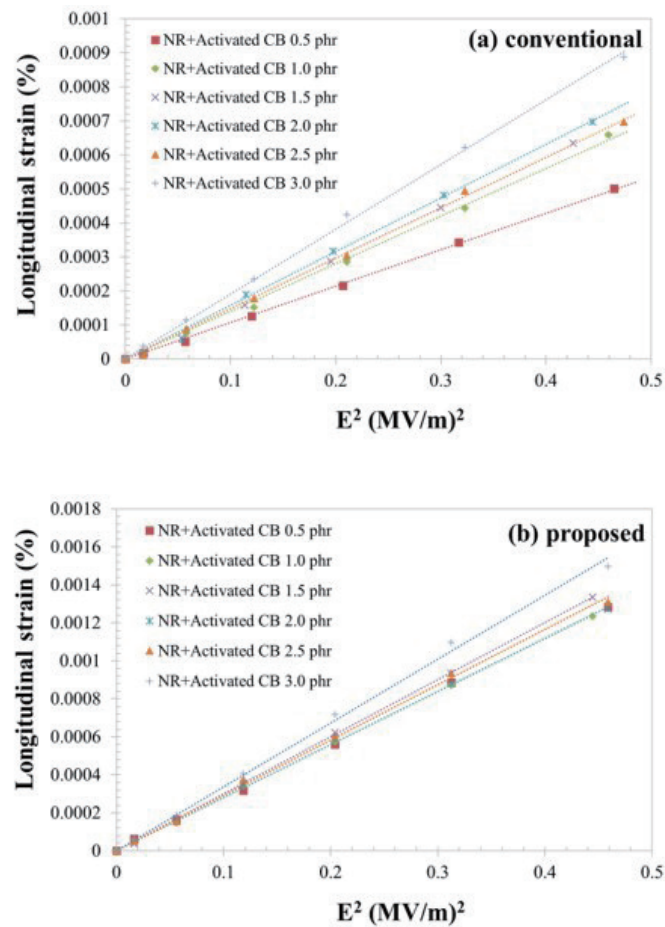

Fig. 3.   (Color online) Longitudinal strain in NR/activated carbon composites prepared by (a) conventional and (b) proposed methods as a function of the square of the electric field at 20 Hz.
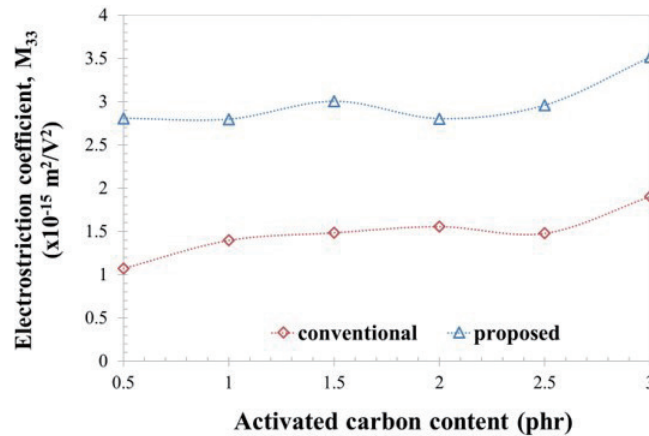
Fig. 4.　(Color online) Electrostriction coefficients of NR/activated carbon prepared by conventional and proposed methods as a function of activated carbon content at 20 Hz.

Table 1
Comparison of relative permittivity, Young's modulus, and M_{33} of different electroactive materials.

Material	ε_r	Y (MPa)	M_{33} (m^2/V^2)	Ref.
PVDF (at 0.4 Hz)	16	2381	2.2×10^{-18}	Eury et al.[9]
PVDF-TrFE (at 0.4 Hz)	11	2500	9.8×10^{-19}	Eury et al.[9]
PU (at 0.1 Hz)	6.6	40	1.0×10^{-15}	Cottinet et al.[10]
PU 1% C (at 0.1 Hz)	15.4	40	4.6×10^{-15}	Cottinet et al.[10]
PU/PANI-EB (at 1 Hz)	13.2	23.22	1.4×10^{-16}	Putson et al.[11]
PU/PANI-ES-HCl (at 1 Hz)	142.6	34.62	7.17×10^{-15}	Putson et al.[11]
PU/PANI (ES) 2% fiber (at 1 Hz)	12661.80	0.32	3.67×10^{-15}	Nawaka et al.[12]
NR/Activated CB 3% (at 20 Hz)	20.48	0.04	3.51×10^{-15}	This work

membranes prepared by the conventional and proposed preparation methods. M_{33} was significantly larger for the composite membranes prepared by the proposed preparation method than for those prepared by the conventional preparation method. Obviously, at the maximum composite ratio (NR+Activated CB 3.0 phr), the longitudinal strain of the proposed preparation method is 1.67 times greater than that of the conventional preparation method. The actuation behaviors of these groups suggest that the preparation method modified between the NR-activated carbon interfaces plays a key role in determining both the electrical and mechanical properties discussed in Sect. 4.2.

　　Table 1 shows a comparison of M_{33} based on dielectric constant and Young's modulus parameters in various electroactive materials. There are three categories for all of the materials. First, polyvinylidene fluoride (PVDF) and PVDF-TrFE had a relatively high modulus, resulting in a lower M_{33}. Second, polyurethane (PU) improves permittivity by forming a composite with conductive materials while maintaining a consistent modulus. The M_{33} of PUs is thousands of times higher than that of PVDF. Lastly, NR has the lowest modulus, although the permittivity can be improved with a conductive material. The findings above suggest that the advantages of NR and activated carbon can be combined to improve the M_{33} performance.

5. Conclusions

An NR-based membrane actuator for use as a material with a low-frequency electrical response is proposed. Two methods were used to prepare NR/activated carbon composite specimens, namely, (1) a conventional preparation method involving the mixing of compounds with an overhead stirrer and (2) a proposed preparation method, which included the addition of Brij. The surface roughness of the rubber membranes obtained by the proposed preparation method was lower than that of the membranes obtained by the conventional preparation method. This result indicates the compatibility between the rubber matrix and the conductive filler. The Young's modulus of the composite membranes increased with the activated carbon content. The Young's modulus of the conventionally prepared specimens was slightly higher than that of the specimens obtained by the proposed preparation method. In addition, the dielectric constant at 20 Hz of the NR/activated carbon membrane was markedly improved by the proposed preparation method. The maximum dielectric constant was 14.12 among the specimens obtained by the conventional preparation method, compared with 20.48 for the specimen with 3.0 phr activated carbon particles obtained by the proposed preparation method. This 1.45-fold increase in maximum dielectric constant was due to the fact that the addition of activated carbon particles enhanced the interfacial polarization. Furthermore, the regular distribution of the carbon filler particles in the rubber matrix increased the permittivity of the composite. The maximum electrostriction coefficient of the NR-filled activated carbon obtained by the proposed preparation method was 3.51×10^{-15} m^2/V^2, which is higher than that of the compound obtained by the conventional preparation method. This strong electrical response is similar to that of a highly responsive modified synthetic polymer material.

Acknowledgments

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About the Author

Darika Jaaoh received her B.S., M.S., and Ph.D. degrees from Prince of Songkla University, Thailand, in 2004, 2009, and 2015, respectively. From 2009 to 2011, she was a lecturer at Yala Rajabhat University, Thailand. Her research interests are in polymer physics, actuators, and sensors. (darika.j@yru.ac.th)