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ELECTROMECHANICAL-CONDUCTIVE NATURAL RUBBER DOPED EGGSHELL AND EGGSHELL MEMBRANE FOR DRUG DELIVERY AND ACTUATOR APPLICATIONS

P. Boonprasert and N. Tangboriboon*

Materials Engineering, Faculty of Engineering, Kasetsart University, Bangkok, 10900, Thailand

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ABSTRACT

Natural rubber composite materials were prepared from vulcanization STR 5L in sulfur curing system by being added with eggshell and eggshell membrane in order to increase electrical and mechanical properties for biomimetic actuator and artificial muscle applications. Samples were vulcanized at temperature 150°C. Hen eggshells and eggshell membrane powder (0, 20, 40, and 60 phr) were added in natural rubber. The main composition of eggshells is calcium carbonate ($CaCO_3$) of high purity more than 96.35 wt% whereas the main composition of eggshell membrane is fibrous protein in terms of collagen. The best condition is addition of eggshell 40 phr (formula 3) and eggshell membrane 20 phr (formula 5) to obtain the highest storage modulus response equal to 2.85 x 10^6 and 2.97 x10^6 Pa, respectively. The curing time (Tc_{90}) of pure natural rubber (formula 1), formula 3, and formula 5 are 8.22, 6.73, and 5.67 min, respectively. Furthermore, the curing time, rheology, and electric field response of natural rubber composite materials are investigate by moving die rheometer and compression set, and the results are reported here.

Keywords: Composites; Eggshell; Eggshell membrane; Electroactive elastomer; Actuator

Author Correspondence, e-mail: fengnnpt@ku.ac.th

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INTRODUCTION

Natural rubber (NR) is an elastomeric material making up of a crosslinked compound comprising of an elastomer and other ingredients [1, 2]. Fillers are important raw materials as a processing aid to provide cost reduction and enhanced physical, thermal, mechanical, and chemical properties. The improvements can be related to the good adhesion at the interface between rubber and well dispersed fillers [3]. Many kinds of fillers are prepared from mineral resources: barite, bauxite, clay, coal, ilmenite, iron ore, monazite, silica, zircon, talcum, mica, wollastonite, and eggshell calcium carbonate, coral, and limestone [4-6]. There are several available sources of calcium carbonate in nature: dolomite, limestone, coral, animal bone, oyster bed, sediment rock, and eggshell. Recently, environmental considerations and public concerns have become important issues as the word strives towards environmental quality and green technology [4]. In minimizing environmental pollution, those natural fillers have various attractive properties as reinforcing agents in natural rubber, namely ease of processing, non-toxicity, a high strength per unit weight, little abrasion, and desirable thermal properties [7]. In particular, egg and egg derivative consumptions produce a great deal amount of daily waste [8-15]. Eggshell, a calcium carbonate ($CaCO_3$) source known as calcite and a stable polymorph at ambient conditions, was chosen here as a filler for the sponge rubber production. Eggshell is known to contain mainly calcium carbonate (94 wt%), organic substances (4 wt%), magnesium carbonate (1 wt%), and calcium phosphate (1 wt%) [16].

The objective of this work was to fabricate natural rubber composites made from dry natural rubber STR 5L as the matrix phase, added with eggshell and eggshell membrane fillers acted as the dispersed phases. Adding eggshell and eggshell membrane affect to increase mechanical and electrical properties characterized by compression set and die rheometry.

MATERIALS AND METHODS

Materials Natural rubber (Standard Thai Rubber 5L or STR 5L) was purchased from Venus Technology Co., Ltd (VTEC), Thailand. NR STR 5L sample is a dry rubber slab with an extra light color, and its dirt content is less than 0.04 wt%. The Mooney viscosity (ML 1'+4') at 100°C, specific gravity, plasticity retention of the NR STR 5L, initial plasticity, and impurity content are 75.2, 0.92 g/cm^3, 51.9, 27.0, and 0.03 wt%, respectively. NR STR 5L has high tensile strength and low levels of non-polymer constituents. Sulfur (S), zinc oxide (ZnO), stearic acid, tetramethylthiuram disulfide (TMTD), and N-cyclohexyl-2-benzothiazolesulphenamide (CBS) were utilized as the vulcanizing agents in the compounded rubber preparation. They were supplied from the Rubber Research Institute, the Department of Agriculture, the Ministry of Agriculture, Thailand. Titanium dioxide (TiO_2), in a form of powder with brilliant whiteness and opaque, was also obtained from the Rubber Research Institute, the Department of Agriculture, the Ministry of Agriculture, Thailand. Chicken eggshells were collected from a local cafeteria. Raw hen eggshells were washed with tap water until the egg white was completely removed and dried at room temperature. The raw hen eggshells were broken into small pieces, crushed by a porcelain mortar and pestle, and ground by a high speed mill with a porcelain ball mill for 60 minutes into a fine powder, and kept in desiccators at room temperature. The chicken eggshells used as eggshell calcium carbonate were cleaned with water and dried at room temperature [17-18]. The eggshells were broken into small pieces by a porcelain mortar and a pestle, then ground by a high speed mill with a porcelain ball mill for 10 minutes into fine powder, and kept fine powder in the desiccator at room temperature.

Table 1. Natural rubber composite samples preparation

Raw materials	Formula 1	Formula 2	Formula 3	Formula 4	Formula 5	Formula 6	Formula 7
NR STR 5L	100	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2	2
Zinc oxide	4	4	4	4	4	4	4
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2
CBS	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Sulfur	2	2	2	2	2	2	2
Eggshell	0	20	40	60	0	0	0
Eggshell membrane	0	0	0	0	20	40	60
Titanium dioxide[5]	5	5	5	5	5	5	5

Remark: Temperature 27°C. Density of natural rubber = 0.92 g/cm^3. Density of eggshell = 2.49 g/cm^3. Density of eggshell membrane = 2.00 g/cm^3.

Instruments: Rheometry is a controlled-strain fluid (Rheometric Scientific Inc., ARES). It was used to investigate the dynamic rheological properties of the composite under controlled strain with a custom-built copper parallel plate geometry 25 mm in diameter attached to insulating spacers which were connected to the transducer or motor. Typical sample thickness or the parallel plate gap was 1.0 ± 0.1 mm. An electric field for the ER measurement was applied using a high-voltage power supply (Keithley, model 2410). Strain sweep tests were first carried out to determine the suitable strains to measure G' and G" in the linear viscoelastic regime. Then the G' and G" of each sample were measured as functions of frequency at various electric field strengths [19]. The composite material samples were pre-sheared for 10 min at a low frequency (0.04 rad/s) with the electric field on in order to attain the equilibrium polarization. Each measurement was carried out at a temperature of 27°C and was repeated at least two or three times. ***True density of samples*** was measured by Gas Pycnometer (Quantachrome, Ultra pycnometer 1000) as following eq.1:

$$\rho = \frac{Weight\ (D)}{True\ volume} \tag{1}$$

where ρ is true density (g/cm^3); D is weight of dry sample (g); and *true volume* is the volume of the solid component only (cm^3). It may be determined by crushing the piece into powder form so that all pores are destroyed and then using a gas pycnometer method. ***The curing behavior*** was investigated at 150°C using moving die rheometer Techpro-Rheo Tech (MDR121105) (Rubber Research Center, Kasetsart University, Thailand). ***Compression set of rubber tests*** was measured according to ASTM D395-03 (Method B) by a compression set (Hampden, APH40). Compression set testing is intended to measure the ability of rubber compounds to retain elastic properties after prolonged action of compressive stresses. The actual stressing service may involve being kept in a definite deflection, the constant application of a known force, or the rapidly repeated deformation and recovery resulting from intermittent compressive forces. Though the latter dynamic stressing, like the others, produces compression set, its effects as a whole are simulated more closely by compression flexing or hysteresis tests. Therefore, compression set testing is considered to be mainly applicable to service conditions involving static stresses. Tests are frequently conducted at elevated temperatures. Calculated compression set are expressed as a percentage of the original deflection as follows:

$$C_B = [(t_o - t_i)/(t_o - t_n)] \times 100 \tag{2}$$

where C_B is compression set (Test Method B) expressed as percentage of the original deflection, t_o is original thickness of specimen, t_i is final thickness of specimen, and t_n is thickness of the spacer bar being used

Sample Preparation of ER Solid: ER solid, with eggshell or eggshell membrane with the percentage by weigth of formula 1 (0 phr), formula 2 (20 phr eggshell), formula 3 (40 phr eggshell), formula 4 (60 phr eggshell), formula 5 (20 phr eggshell membrane), formula 6 (40 phr eggshell membrane), and formula 7 (60 phr eggshell membrane) were respectively prepared. Table 1 shows the weight composition of raw materials for natural rubber composite materials preparation composed of natural rubber, stearic acid, zinc oxide, tetramethyl thiuram disulfide (TMTD), benzothiazyl-2-cyclohexyl-sulfenamide (CBS), sulfur (S), titanium dioxide (TiO_2), eggshell, and eggshell membrane having the unit in terms of parts per hundred rubber (phr). The raw materials of natural rubber composite materials were prepared using a two-roll mill (Mitsubishi, model R11-3FF). The natural rubber composite materials were vulcanized in sulfur curing system at 150°C to obtain a 90% cured reaction (t_{90}), by the rheometer cure curves.

RESULTS AND DISCUSSION

Characteristics and mechanical properties (Mooney viscosity, curing time, and compression set) of NR composite materials were measured according to ISO 289-1, ASTM D5289, and ASTM D395 (method B), respectively, and the obtained data are shown in Table 2. The NR composite materials with the fillers (eggshell and eggshell membrane) have short scorch times and curing times. The Mooney viscosity values of the natural composites increase when the amount of filler added into the NR increases. The NR composite with 40 phr eggshell (formula 3) is found to possess the highest storage modulus at 1.5 kV/mm equal to 2.85×10^6 Pa as shown in Fig. 1 and a good compression set 23.1% as can be seen from the data shown in Table 2. On the other hand, the NR composite with 20 phr eggshell membrane (formula 2) possesses the highest storage modulus at 1.5 kV/mm equal to 2.97×10^6 Pa as shown in Fig. 2 with a good compression set 26.3% as can be ssen from the data shown in Table 2.

Table 2. Characteristics of vulcanization natural rubber composite samples at 150°C

Properties	Formula 1	Formula 2	Formula 3	Formula 4	Formula 5	Formula 6	Formula 7
Mooney viscosity (ML 1'+4') 100°C	45.8	49.5	54.4	55.5	49.6	55.0	59.7
Initial vulcanization at 121°C, t_5 (min)	30.05	26.12	23.20	19.11	21.49	18.32	16.29
Initial vulcanization at 121°C, t_{35} (min)	32.59	29.07	25.35	21.25	24.07	20.39	18.10
Ts_1[a]	5.79	4.93	4.35	4.13	3.18	2.96	2.75
Ts_2[b]	6.26	5.33	4.72	4.45	3.55	3.28	3.04
Tc_{10}[c]	5.42	4.63	4.14	3.98	2.94	2.79	2.61
Tc_{50}[d]	6.38	5.54	5.04	4.84	3.77	3.56	3.38
MDR Type, TECH PRO Arc 0.5°, 150°C, t_{90} (min) or Tc_{90}[e]	8.22	7.17	6.73	6.34	5.67	4.98	4.75
Tc_{95}[f]	9.14	8.04	7.62	7.13	6.65	5.58	5.29
Tc_{100}[g]	14.21	12.43	12.52	11.05	13.47	9.82	8.27
Compression set at 70°C, 22 h. (%)	22.6	22.3	23.1	23.3	26.3	26.3	29.9

Remark: Mooney viscosity (ML 1'+4') 100°C of pure STR 5L is 45.8 measured according to ISO 289-1.

[a] means scorch time: time required for the increase of point 1 (Ts_1) from minimum torque or in order to indicate time required for the beginning of the crosslink process.

[b] means scorch time: time required for the increase of point 2 (Ts_2) from minimum torque or in order to indicate time required for the beginning of the crosslink process.

[c] means time corresponding to 10% curing measured according to ASTM D 5289.

[d] means time corresponding to 50% curing measured according to ASTM D 5289.

[e] means time corresponding to 90% curing or optimum vulcanization time measured according to ASTM D 5289.

[f] means time corresponding to 95% curing or optimum vulcanization time measured according to ASTM D 5289.

[g] means time corresponding to 100% curing or optimum vulcanization time measured according to ASTM D 5289.

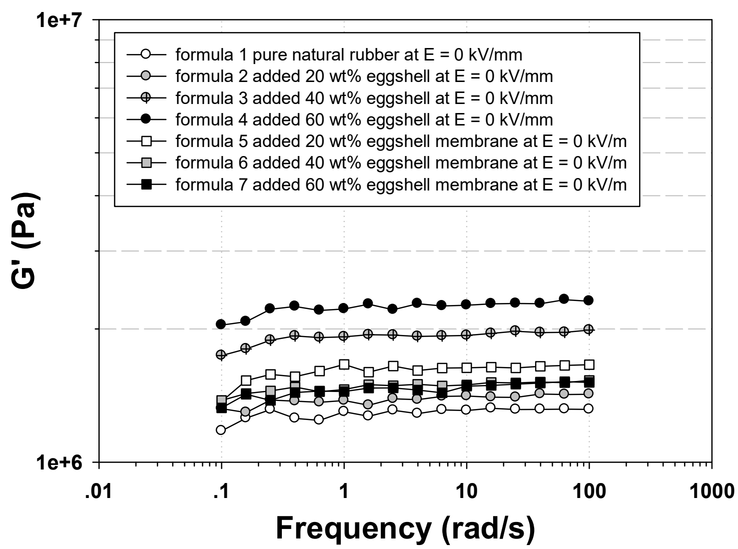

Fig.1. Storage modulus of NR composite samples at E = 0 kV/mm.

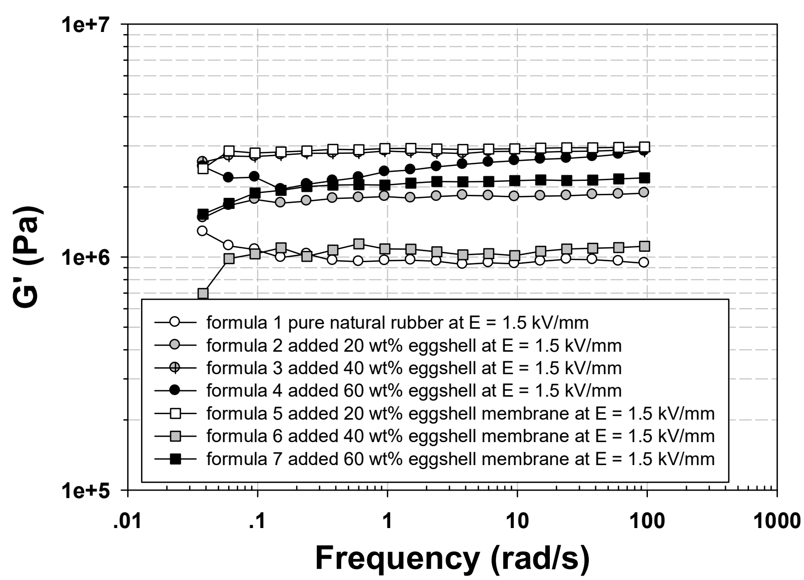

Fig.2. Storage modulus of NR composite samples at E = 1.5 kV/mm.

Table 3. Rheological properties of NR composite materials (STR 5L) with/without adding fillers (eggshell and eggshell membrane) measured at 1 rad/s and at 27°C

Samples	Filler adding (phr)	G_0' (Pa)	$G_{1.5\ kV/mm}$ (Pa)	$\Delta G'_{1.5\ kV/mm}$ (Pa)
Formula 1 (pure NR)	0	1.32×10^6	9.41×10^5	3.75×10^5
Formula 2 (eggshell)	20	1.42×10^6	1.88×10^6	4.58×10^5
Formula 3 (eggshell)	**40**	**1.99×10^6**	**2.84×10^6**	**8.56×10^5**
Formula 4 (eggshell)	60	2.31×10^6	2.87×10^6	5.64×10^5
Formula5(eggshell membrane)	**20**	**1.66×10^6**	**2.97×10^6**	**1.31×10^6**
Formula 6 (eggshell membrane)	40	1.53×10^6	1.11×10^6	4.18×10^5
Formula 7 (eggshell membrane)	60	1.51×10^6	2.19×10^6	6.72×10^5

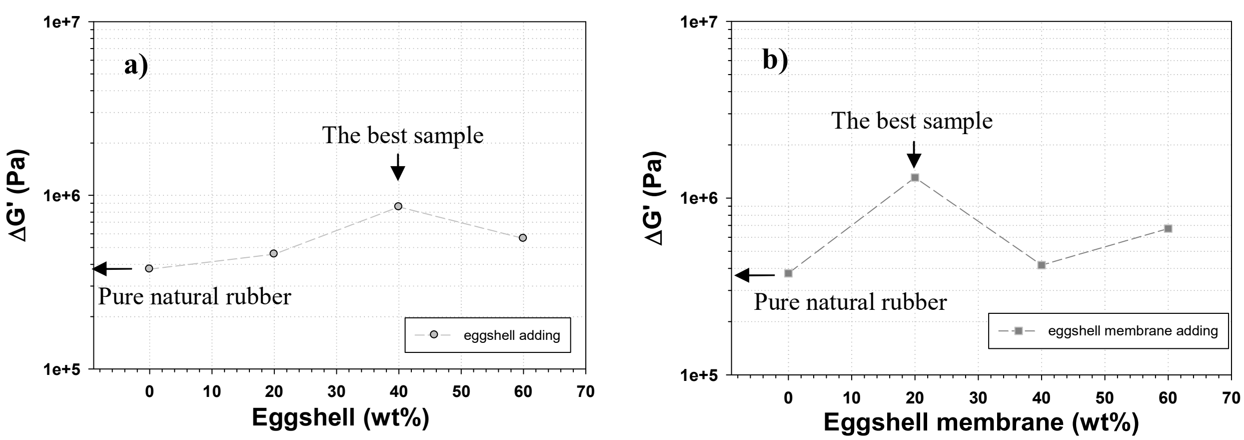

Fig. 3. Storage modulus response, ΔG' (1 Hz, 1.5 kV/mm) and G_0' (1 Hz) of pure natural rubber at 27°C of: a) natural rubber composite materials with/without adding eggshell; and b) natural rubber composite materials with/without adding eggshell membrane.

Figs. 3a and 3b show the corresponding storage modulus response $\Delta G_0'$ (1Hz) of NR composites vs amount of fillers (eggshell and eggshell membrane) at an electric field strength of 1.5 kV/mm. Both figures of the corresponding storage modulus response ($\Delta G_0'$) appear to increase drastically with amount of filler adding: eggshell adding from 3.75×10^5 Pa (formula 1) to 8.56×10^5 Pa (formula 3) and eggshell membrane adding from 3.75×10^5 Pa (formula 1) to 1.31×10^6 Pa (formula 5) as can be seen from the data shown in Table 3. The increase $\Delta G_0'$ with the weight percentage of particle eggshell and eggshell membrane can be attributed to the effect of eggshell and eggshell membrane particles acting as reinforcing fillers. Formula 3 (40 wt% eggshell) and formula 5 (20 wt% eggshell membrane are a dielectric materials that can store or absorb additional forces or stresses within the matrix. Therefore both formula 3 and 5 show the highest sensitivity. Parthasarathy and Klingenberg pointed out that the electro-rheological (ER) response is strongly influenced by electrostatic and repulsive interactions at smaller particle separations. Conductivity differences between the natural rubber and the eggshell and eggshell membrane particles generally control the polarization, and hence the ER properties, under DC electrical field.

CONCLUSION

Our results suggest that eggshell and eggshell membrane powder acted as a bio-filler can be used to absorb an energy loss and to store additional elastic energy within the natural rubber matrix. The main composition of eggshell is calcium carbonate ($CaCO_3$) which is a ceramic material or inorganic matter while the main composition of eggshell membrane composed of fibrous protein namely collagen mixed with small amount of calcite ($CaCO_3$). They can induce spontaneous polarizations (electronic, ionic, and orientation) through the positioning of Ca^{2+}, CO_3^{2-}, NH_3^+, and $CO\text{-}N^+H_2$. The ER properties—G', G'', and ΔG'—under the oscillatory shear mode of NR composite materials were investigated as functions of electric field strength and filler particle adding. With and without an electric field, the dynamic moduli G_0', $G'_{1.5\ kV/mm}$, and $\Delta G'_{1.5\ kV/mm}$ of formula 3 (40 phr eggshell adding) are 1988500, 2844700, and 8.56×10^5 Pa, respectively. The dynamic moduli G_0', $G'_{1.5\ kV/mm}$, and $\Delta G'_{1.5\ kV/mm}$ of formula 5 (20 phr eggshell membrane adding) are 1660300, 2967900, and 1.31×10^5 Pa, respectively. Therefore, both eggshell and eggshell membrane are potential candidates for used as additives for NR composites to make bio-mimetric actuators and/or artificial muscles due to many advantages i.e. soft, flexible, low cost, green material, nontoxic, and fast curing within 6-7 min at 150°C.

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