Microwave Absorbing Rubber Composites Containing Carbon Black and Aluminum Powder

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ABSTRACT: Natural rubber (NR), epoxidized natural rubber (ENR), and chlorosulfonated polyethylene (CSM) composites filled with conductive carbon black and aluminum powder have been prepared by using a two-roll mill. An electromagnetic interference shielding effectiveness of those rubber composites was carried out in the frequency range of 8–12 GHz (X-band microwave). The increase of filler loading enhanced shielding effectiveness of the rubber composites. Conductive carbon black was more effective in shielding than aluminum powder. Binary filler-filled rubber composites showed higher shielding effectiveness than that of single filler-filled rubber composites. It has been observed that the shielding effectiveness of these rubber composites could be ranked in the following order: ENR ≥ CSM > NR, whereas the mechanical properties of the rubber composites were in the order of CSM > ENR > NR. The correlation between shielding effectiveness and electrical conductivity as well as mechanical properties of the rubber composites are also discussed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2036–2045, 2007

Key words: shielding effectiveness; rubber composites; natural rubber; radar; microwave

INTRODUCTION

Electrically conductive polymer composites have attracted a great deal of scientific and commercial interest. The mechanism of electrical conduction in these composites is the formation of a continuous network of conductive fillers throughout the insulating polymer matrix. These conductive composites have been widely used in the area of electromagnetic/radio-frequency interference (EMI/RFI) shielding, electrostatic discharge (ESD), conductive adhesives for die attach in electronic packaging applications, and elastomer interconnect devices used for integrated circuit (IC) package assembly.[1] Electrically conductive elastomer composites, which exhibit variable conductivity in response to varying external loading, are widely used for various electronic applications, touch control switches and strain and pressure sensors for applications such as robot hands or artificial limbs.[1] Gaskets made from electrically conductive rubber composites have attracted much attention as a means for preventing EMI radiation leakage.

Polymers as electrical insulators are transparent to electromagnetic radiation and thus do not provide EMI shielding. Electrical conductivity is a prerequisite for EMI shielding effectiveness (SE). Both conductivity and EMI SE can be improved by the incorporation of conductive fillers in a polymer matrix. The most economic process of manufacturing shielding material is the addition of conductive fillers into the polymer matrix to generate conductive composites. Depending on SE at different frequency ranges, these materials are considered for use in different microelectronic devices and microwave applications, such as absorbing materials. The addition of metal in the form of powder, flake, and fiber in the polymer matrix increases the conductivity of the system and by that provides effective EMI shielding. To improve the SE of composites, metal coated fibers were applied, such as aluminum or nickel coated carbon or glass fiber and nickel coated mica. Polyaniline, short carbon fiber, carbon nanotube and conductive carbon black have been studied for this application. Conductive rubber composites in EMI shielding application have been reported and include nitrile rubber (NBR),[2] polychloroprene (CR),[3,4] silicone,[5–7] polyurethane,[8] butyl rubber (IIR),[9,10] polysulfide polymer,[11] ethylene vinyl acetate (EVA),[12–15] EVA blended with natural rubber (NR),[15] ethylene–propylene–diene monomer (EPDM),[13,16] EVA/EPDM blends,[13] and EVA/ethylene–propylene–ethylidenenorbornene blend.[14] Conductive fillers named in those reports included conductive carbon black,[2,10,12–16] short carbon fiber,[2–4,12–15] graphite particles,[5,11] polyaniline,[6,8] boron carbide,[9,16] nickel fiber,[11] and ferrite particles.[7,17,18] Some researchers had been studied NR composites such as

TABLE I
Typical Properties of Ketjenblack® EC-300J

Property	Value
DBP water absorption ratio	360 mL/100g
Pore volume	1.15 cm^3/g
Porosity	69.3%
Specific surface area	950 m^2/g
Apparent bulk density	0.130 g/cm^3
Grain size	365 Å
Typical resistivity	0.341 Ω cm

conductive carbon black-filled NR for pressure sensor,[19] B$_4$C-filled NR for thermal neutron radiation shields,[20] and zinc ferrite-filled NR.[17,18] Electrical properties of rubber composites filled with conductive carbon black have been reported.[21–23] The objective of this research is to prepare rubber composites from natural rubber, epoxidized natural rubber, and chlorosulfonated polyethylene for EMI shielding application. SE in the frequency range of 8–12 GHz and mechanical and electrical properties of the rubber composites will be also reported.

EXPERIMENTAL

Materials

All ingredients were commercial grade and used as received. The natural rubber (NR) was STR5L grade, produced in Thailand. Its Mooney viscosity was 72 [ML(1 + 4) at 100°C]. Epoxidized natural rubber, Epoxyprene®50 (ENR50), was produced by Muang Mai Guthrie Public Co. Ltd., Thailand. It consisted of 50 mol % of epoxidation with a Mooney viscosity of 89 [ML(1 + 4) at 100°C]. Chlorosulfonated polyethylene (CSM) used was Hypalon®40, produced by DuPont Dow Elastomer Co. Ltd. Its Mooney viscosity was 63 [ML(1 + 4) at 100°C]. It contains 34.40% chlorine and 0.98% sulfur, by weight. Sulfonyl chloride group (SO$_2$Cl) is a reactive site for crosslink reaction. Ketjenblack® EC-300J conductive carbon black was produced by Akzo Nobel. Typical properties are listed in Table I. Aluminum powder used was Lunar® Al-V95, produced by Siam Prodex Co., Thailand. The mean particle diameter was 30 μm. Sieve analysis was + 325 mesh, 2% maximum on 44 μm screen. Typical resistivity was 2.824 μΩ cm and typical density was 2.70 g/cm^3. It is flake lamellar structure and particle thickness was less than 0.2 μm. Leafing content was 69% and water coverage was 15,000 cm^2/g.

Preparation of rubber composites

Rubber compounds were mixed on a two-roll mill (Kao Tieh KT7014). Formulations of the rubber compounds are shown in Table II. The 1.5-mm thick slabs

were then press-cured at 150 °C under a pressure of 150 kg/cm^2. Vulcanization time was determined by using a moving die rheometer (Alpha Technology MDR2000). Masterbatch of conductive carbon black was prepared by using an kneader type internal mixer (Yong Fong machinery Co., Ltd.). Sample designation refers to the type of rubber followed by carbon black content and aluminum powder content, i.e., NR 50/30 = natural rubber containing 50 phr of carbon black and 30 phr of aluminum powder, ENR 30/0 = epoxidized natural rubber containing 30 phr of carbon black, and CSM 0/30 = CSM containing 30 phr of aluminum powder.

Measurement of shielding effectiveness

Electromagnetic interference (EMI) shielding effectiveness (SE) was measured in the frequency range of 8–12 GHz. According to EN50147-1, the European standard test method, the distance between signal generator (transmitting antenna) and signal detector (receiving antenna) was 60 cm, and the specimen was placed midway perpendicular to both antennas. A schematic diagram of EMI SE experiment set up is shown in Figure 1. Specimen size was calculated according to the "3-dB beam width" measurement.[24,25] The setup of SE measurement consisted of a signal generator (Hewlett-Packard HP83620B), a power meter (Agilent 53147A) and a power sensor (Agilent 8485A). Horn antennas (width × length, 7 cm × 7 cm) were applied for both the transmitting and the receiving antenna. The specimen was fixed

TABLE II
Compound Formulation

Ingredient	Loading (phr^a)		
	NR	ENR	CSM
Rubber	100	100	100
Zinc oxide	5	5	–
Stearic acid	2	2	2
CBS^b	1.2	1.5	–
Wingstay® L^c	1.0	1.0	–
Sulfur	2.0	2.0	–
Calcium stearate	–	3.0	–
Magnesium oxide^d	–	–	4.0
PE-200^e	–	–	3.0
Tetrone®A^f	–	–	2.0
MBTS^g	–	–	1.5
Ketjenblack®EC-300J	0, 30, 50	0, 30, 50	0, 30, 50
Aluminum powders	0, 30, 50	0, 30, 50	0, 30, 50

^{a} Phr: Parts per hundred of rubber.
^{b} N-cyclohexyl-2-benzothiazyl sulphenamide.
^{c} Butylated reaction product of p-cresol and dicyclopentadiene.
^{d} Maglite®D (magnesia).
^{e} Entaerythritol, Hercules®.
^{f} Dipentamethylene thiuram tetrasulfide.
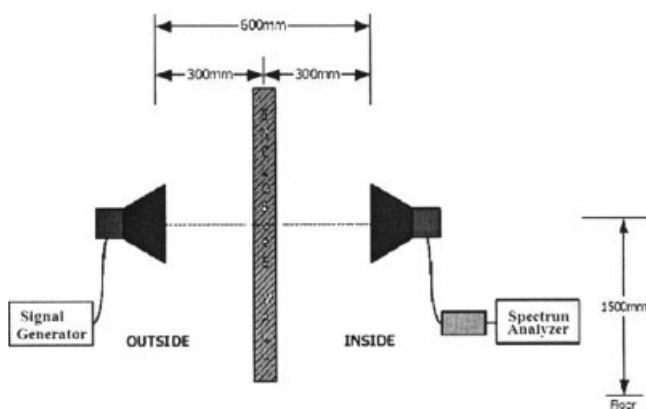^{g} Mercapto benzo thiazole sulfide.

Figure 1 A schematic diagram of EMI SE measurement set-up.

on a wooden holder by using paper pressured-adhesive. NR containing 30 phr of carbon black (NR30/0) was used as a reference for every SE measurement to check the consistency of the measurement. Some noise was appeared when SE was greater than 45 dB.

Scanning electron microscopy analysis

Freeze fractured surface of rubber composites was observed by using a scanning electron microscope (JEOL JSM5800LV) to investigate distribution of aluminum powder. The specimens was determined without gold- or carbon-coating. X-ray mapping of aluminum element on the specimen surface was investigated.

Measurement of electrical conductivity

Electrical conductivity was measured by using a custom-made four-point probe conductivity meter.[26] The specific electric conductivity σ (S/cm) values of the rubber composite sheets were obtained by measuring the bulk resistances R (Ω). The relation $\partial = (1/Rt)(1/K)$ was used to calculate the specific electric conductivity, where t is the specimen thickness and K is the geometric correction factor which is equal to the ratio w/L, where w and l are the probe width and the length respectively. The K value was determined by calibrating the four-point probe with a standard metal sheet with a known specific resistivity. Applied DC currents were sufficient low to be in the linear Ohmic regime.

Testing of physical and mechanical properties

Tensile testing and tear resistance were conducted at a speed of 500 mm/min according to ASTM D412 and ASTM D624 respectively, by using a universal testing machine (LLOYD 1000S). Thermal aging was operated at 100°C for 48 h by using a gear oven and

changes in tensile properties were calculated according to ASTM D573. The aging resistance is expressed as a percentage of the change in tensile properties calculated as follows:

$$P = [(A - O)/O] \times 100$$

where P is the percentage change in the property, O is the original value, and A is the value after aging. Increases are indicated as positive and *vice versa*. Compression set was carried out according to ASTM D395. The 12-mm thick cylindrical specimens were prepared and compressed to 25% of original height for 22 h at 27 and 70°C. Specimens were then released from the press and left on the table at ambient environment (27°C) for 30 min to equilibrate before measuring the height. Three specimens were tested for each sample. The hardness Shore A of rubber composites was measured according to ASTM D2240 on the 12-mm thick cylindrical specimens.

RESULTS AND DISCUSSION

Theory of shielding effectiveness

According to ASTM D4935, shielding effectiveness (SE) is the ratio of power received with and without a material present for the same incident power. It is usually expressed in decibels by the following equation:

$$\text{SE} = 10 \log \frac{P_1}{P_2} \text{ (decibels, dB)}$$

where P_1 is the received power with the material present and P_2 is the received power without the material present.

EMI shielding is the result of reflection (R), absorption (A), and internal multiple reflection (I) of the incident electromagnetic waves in the samples. These three quantities are related to each other by the following expression for SE:

$$\text{SE} = 10 \log \frac{P_1}{P_2} = (R + A + I)$$

I is negligible when A is over 10 dB[2] or $\geq$ 15 dB.[15] R and A are given by the following equation:[15]

$$R = 108 + \log(G/\mu f)$$

and

$$A = 1.32 \, t\sqrt{G\mu f}$$

where G is the conductivity of the samples relative to copper, μ is the magnetic permeability of the sample relative to vacuum or copper (μ is usually 1.0), f is the

Frequency (GHz)	Shielding effectiveness (dB)				
	Run 1st	Run 2nd	Run 3rd	Run 4th	Avg. ± SD
8.5	14.84	14.87	14.24	14.57	14.63 ± 0.29
9.0	14.32	14.34	14.09	13.42	14.04 ± 0.43
9.5	14.42	14.67	14.10	14.84	14.51 ± 0.32
10.0	14.10	14.86	14.77	14.76	14.62 ± 0.35
10.5	14.19	14.37	14.87	14.52	14.49 ± 0.29
11.0	14.18	14.27	14.16	12.94	13.89 ± 0.63
11.5	14.21	14.23	14.71	15.70	14.71 ± 0.70
12.0	15.15	14.97	15.10	15.18	15.10 ± 0.09

frequency of radiation in MHz, and t is the thickness of the sample in cm. The influence of all parameters (G, μ, f, and t) in the SE depends on the type of shielding, reflection or absorption shielding. Due to the experimental inadequacy of this study it was not possible to measure the contribution towards SE of different phenomena separately.

Specimen size and reproducibility

When it is required to transmit energy efficiently into space, a device called an "antenna" is used. The horn is a simple form of antenna. As in most microwave applications, it required as much energy as possible to be radiated in a particular direction, therefore the horn is used. The directional characteristics of an antenna, called "radiation pattern" or "polar diagram," vary in many ways, also from a single lobe to several lobes. Most energy is concentrated into the main lobe. The 3-dB beam width is used as a measure of the directivity of the antenna and the width of the main lobe. It is the angle between the two points on the main lobe at which the radiated power density is half the maximum. Based on the "3-dB beam width" measurement the specimen size should be 15 cm × 15 cm. However, the specimen size used in this study was 30 cm × 30 cm to ensure that the specimen was sufficiently large.

The SE measurement was operated several times and each time may yield different results due to electronic device characteristics, operator errors, measurement-system errors, and specimen-caused errors. To investigate reproducibility or uncertainty of each measurement, the NR30/0 specimen, containing 30 phr of carbon black, was used as a control specimen for every measurement. Their SE values are listed in Table III. SE values of all tests at each frequency were similar. The standard deviation of all measurement for both specimens proved to be less than ± 1.0 dB, indicating an acceptable accuracy for every test measurement. Obviously, the SE values of this sample was 14–15 dB in the X-band microwave (8–12 GHz).

Shielding effectiveness of rubber composites

The SE of rubber composites containing single-filler, carbon black, or aluminum powder, is shown in Figure 2. As stated earlier, sample designation is name of rubber followed by carbon black content and aluminum powder content respectively. All unfilled rubbers showed very low SE, < 1 dB. The 50 phr of carbon black increased SE of the rubber composites (50/0 samples) up to 18 dB, 28 Db, and 25 dB for NR, ENR, and CSM respectively. In contrast, the maximum SE of rubber composites containing 50 phr of aluminum powder (0/50 samples) was 10 dB. SE increased with filler content and carbon black was more effective
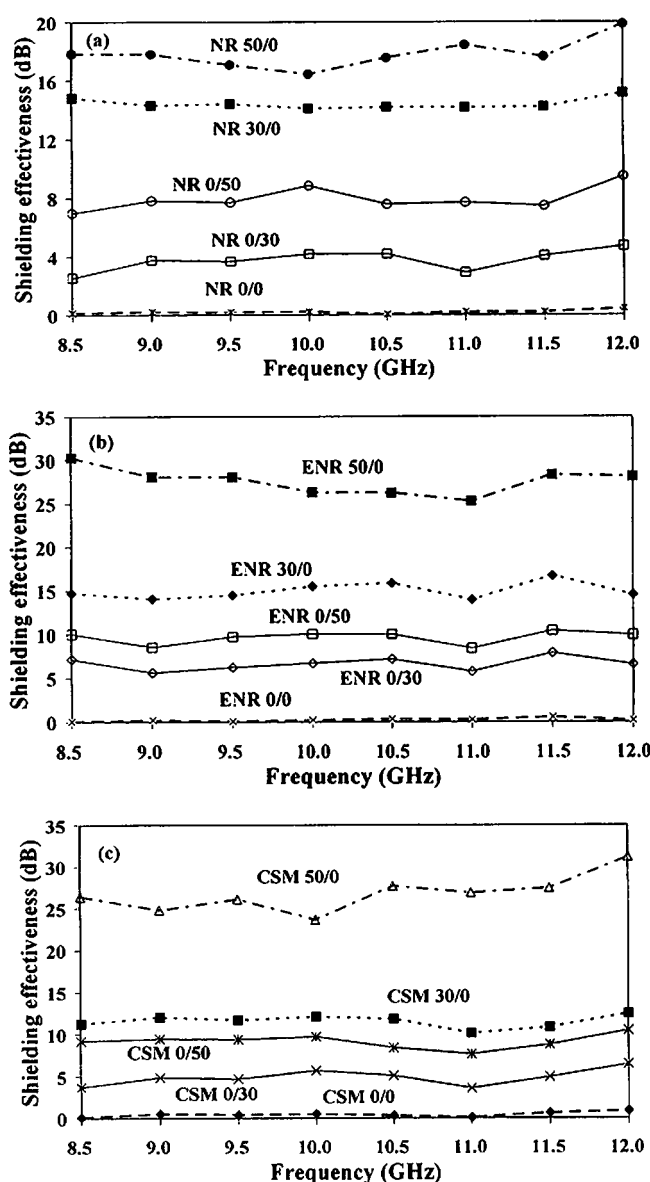

Figure 2 Effect of single-filler on SE: (a) NR composites; (b) ENR composites; (c) CSM composites. The former number represents carbon black content and the latter number represents aluminum powder content.

than aluminum powder in providing higher EMI shielding. The highest SE of these rubber composites could be ranked in the following order: ENR ≥ CSM > NR.

Generally speaking, SE of each sample was in the same range under the entire frequencies (8.5–12 GHz) and the effect of fillers on SE of three rubber systems was similar. The EMI SE of carbon black-filled rubber composites (50/0 samples) in the present study (18–28 dB) was higher than other rubber composites containing 50–60 phr of conductive carbon black, i.e., nitril rubber (12 dB),[2] EVA (18 dB),[12,13] NR (10 dB),[15] EPDM (8–10 dB)[13,16] and EVA/EPDM blend (22.5 dB).[13] Ghosh and Chakrabarti[16] proposed that for high EMI SE, EPDM vulcanizates containing ≥ 50 phr of conductive carbon black were indicated to be quite effective and useful. There are many factors affecting the EMI SE, such as conductivity or polarity of rubbers and conductive fillers, filler content, particle size/shape and other characteristics of conductive fillers, filler content, filler dispersion and distribution, specimen size and shape, and testing method. It should be noted that the conductivity of rubber compounds not only depends on filler's conductivity but also depends on efficiency of mixing. In this study, some agglomerates may not break down. Another factor may come from the fact that processing oil coated on the carbon black's surface during mixing. Therefore, conductivity of rubber compounds were not high as expected. Pramanic et al.[2] showed the effect of filler shape and filler content. The 10 phr short carbon fiber gave comparable SE as that of 60 phr conductive carbon black (Conductex[TM] 900) and 60 phr conductive carbon black still showed higher SE and conductivity than that of 50 phr conductive carbon black.

Undoubtedly, non polar polymers should show lower SE than polar polymers. This may be attributed to higher SE of black-filled ENR and CSM in the present study compared to nitril rubber, EVA and EVA/EPDM blend of those works. High SE of black-filled NR in the present study, compared to the previous work,[15] arose from many factors as mentioned above. They[15] used different conductive carbon black (Vulcan[®] XC-72) and different testing method from the present study. Different filler could provide different characteristics, particularly conductivity and surface activity. Differences in rubber compounding method resulted in differences in filler distribution and dispersion and different testing SE measurement may give a different result.

To enhance SE combination of both fillers, as called binary-filler, was applied to the rubber. It is well established that SE depends not only on the conductivity but also on the reflection and absorption coefficient of the dispersed filler and its size, shape, and distribution in the matrix. The distribution of filler in

the matrix governs the space between filler aggregates. To achieve high shielding, the conductive filler particle should form a closely-packed array throughout the matrix so that filler particles would be arranged more like a conducting mesh that could be used as EMI shielding.[2] In the binary filler-filled rubber composites, carbon black aggregates can bridge the gap between two aluminum powders. Binary-filler system offered synergistic behavior as shown in Figure 3. The average SE of the 50/50 samples was 30 dB, 40 dB, and 35 dB for NR, ENR, and CSM respectively. The efficiency of SE was improved by 40–67% in comparison with the 50/0 samples. ENR still showed highest SE and slightly higher than CSM,
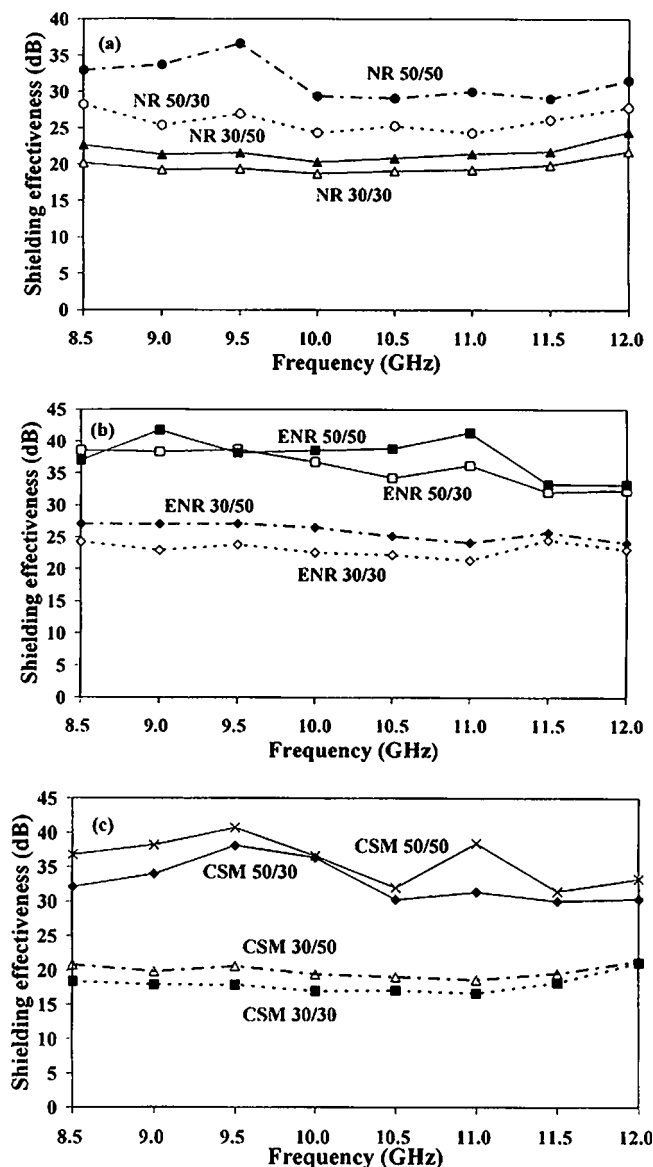
Figure 3 Effect of binary-filler on SE: (a) NR composites; (b) ENR composites; (c) CSM composites. The former number represents carbon black content and the latter number represents aluminum powder content.
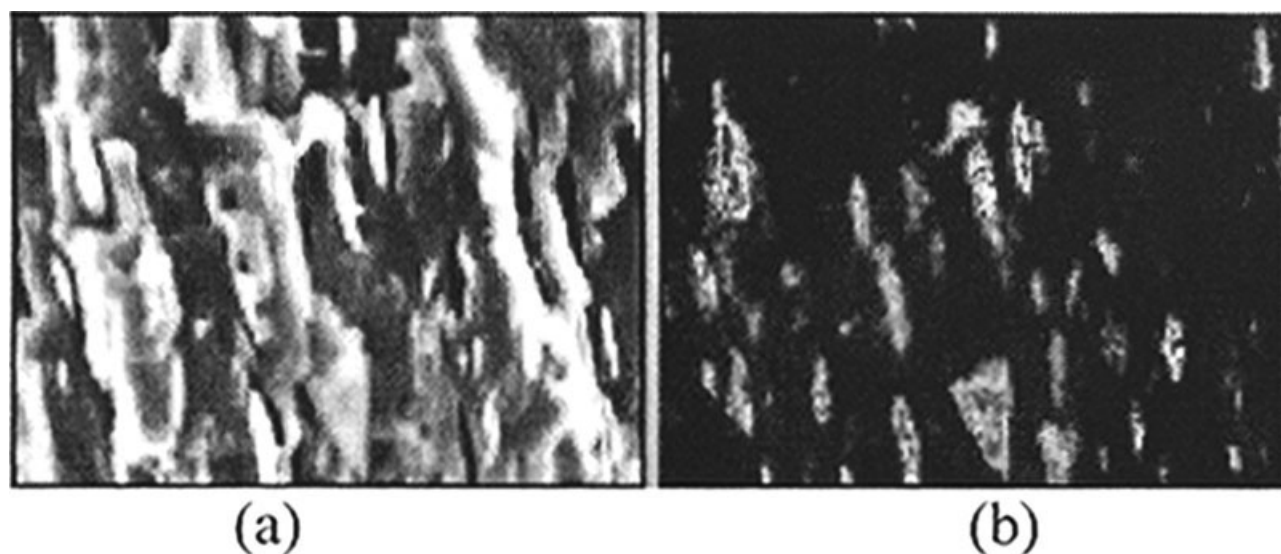
Figure 4 (a) SEM micrographs of NR composites containing 50 phr of carbon black and 50 phr of aluminum powder; (b) X-ray mapping micrograph showing aluminum element of figure (a).

whereas NR remained the lowest SE rubber composites. However, if the aluminum powder distribution was not even, SE of the rubber composites would not increase as much as it could be. Distribution of aluminum powder in NR composite (50/50 sample) is shown in Figure 4. Cylindrical shape of the powder and well distribution are observed. It should be noted that this sample could be observed under SEM without gold-coating. This indicates good electrical conductivity.

The 50 phr of aluminum powder (0/50 samples) could increase SE of the specimens up to 8–10 dB. Addition of both fillers provided higher SE than that of single-filler. The maximum SE of binary filler-filled specimens was 36.66 dB, 41.74 dB, and 40.73 dB for NR, ENR, and CSM respectively. Although aluminum is more conductive than conductive carbon black, the density of aluminum is much higher than that of conductive carbon black. As a result, the volume fraction of aluminum powder was much lower than that of carbon black, with regard to similar weight fraction. Furthermore, grain size of carbon black is of the order of nanometers whereas the particle size of aluminum powder is in micrometer-scale. These attribute to different conductivity of the rubber composites which is one of the important parameters controlling shielding characteristics of materials. Therefore, conductivity of rubber composites containing 50 phr of aluminum powder was lower than those containing 50 phr of carbon black, causing to lower the SE in the 0/50 samples. Although the maximum SE of three rubber composites fell in the same range, ENR composites tended to show highest SE and NR composites is the lowest rank. Undoubtedly, polar rubber (ENR and CSM) exhibited higher SE than nonpolar rubber (NR).

This is due to the higher conductivity of ENR and CSM as will be discussed later.

Electrical conductivity

Electrical conductivity from four-point probe measurement of rubber composites is represented in Table IV. NR showed very low conductivity (1×10^{-17} S/cm), corresponding to a typical insulator. The dielectric constant of unfilled rubber was 2.71, 5.43, and 7.89 for NR, ENR, and CSM respectively. By adding 50 phr of aluminum powder, conductivity increased approximately 10 times (1.16×10^{-16} S/cm). The much increase in conductivity was derived by using carbon black. The value was in the range of 10^{-8} S/cm for NR composites and 10^{-6} S/cm for ENR and CSM composites. Binary-filler specimens (50/50 samples) showed significant increase in conductivity of NR composites compared with the black-filled specimens. Conductivity of the binary filler-filled ENR and CSM composites were in the same range as the black-filled specimens. Job et al.[19] had already reported

TABLE IV
Electrical Conductivity (S/cm) of the Rubber Composites

[CB]/[AL][a]	NR	ENR	CSM
0/0	1.00×10^{-17}	–	–
50/0	1.16×10^{-8}	1.03×10^{-6}	9.17×10^{-6}
0/50	8.37×10^{-16}	8.54×10^{-13}	4.50×10^{-13}
50/30	1.13×10^{-8}	5.37×10^{-6}	9.36×10^{-6}
50/50	4.85×10^{-7}	3.73×10^{-6}	9.32×10^{-6}

[a] Ratio in phr, [CB] = carbon black, [AL] = aluminum powder.

conductivity of NR (2×10^{-10} S/cm) and NR filled with 25 phr of conductive carbon black (5×10^{-2} S/cm). Their results were much higher than the present results. This may be due to differences in conductivity measurement and sample preparation. It was found that significant increase in conductivity of rubber composites would be derived when conductive black was 50 phr or more.[21]

It was clear that NR composites had lower conductivity than ENR and CSM composites. Based on the dielectric constant and impedance from preliminary study, unfilled NR also showed lower conductivity than the other two rubbers. As stated earlier, there are many factors controlling conductivity of rubber composites, viscosity of rubber is another factor should be concerned. However, Mooney viscosity (MV) of rubbers in this work did not relate to the conductivity of black-filled rubber. ENR showed higher MV and higher conductivity than NR whereas CSM showed lower MV and higher conductivity than NR. This indicated that intrinsic conductivity of rubber played more important role than rubber viscosity.

It is well established that SE of a conductive composite is related to its conductivity. Conductivity is dependent on the polymer matrix, the type and concentration of conductive fillers, the dispersion quality of the compound, the formation of a continuous conductive network in the polymer matrix and the distribution of the fillers during processing. The incorporation of carbon black in the rubber matrix imparted higher conductivity compared to aluminum powder at the same filler loading. This is because of differences in volume fraction and grain size as stated earlier. The formation of conductive networks is prerequisite. Regarding to shape and size of aluminum powder, it was more difficult to build good conductive network in the rubber, compared to the carbon black, resulting in a marginal increase in conductivity, i.e., the 0/50 samples. The conductivity of an insulator filled with conductive particles is explained by percolation theory and the threshold formation of conductive networks can be well described by this theory.[21] Sau et al.[21] mentioned that the region of rapid conductivity increase was called the percolation region. Further increasing the filler loading beyond the percolation region caused little change in the conductivity of the rubber composites. At a low level of carbon black the electrical conductivity was governed by the rubber matrix between the particles. The distance between the black particles was very high, the electrical conductive path was discontinuous. At higher level of carbon black the distance between the particles decreased and discrete chain structures formed in the small gaps. As the number of filler particles increased the number of continuous chains or conductive paths through rubber matrix increased. At the percolation region a continuous conductive chain was formed

and electrical conductivity was stable. The conduction through the bulk of rubber composites was controlled by conduction over a number of paths of a randomly formed chain of particles. It is believed that the conductive paths occurred in the present rubber composites and more effective path was obtained from carbon black, but, unfortunately, it was unable to identify the location of the percolation region in the present study because unability to prepare masterbatch containing > 50 phr conductive carbon black. Due to Pramanic et al.,[2] 60 phr conductive carbon black still showed higher SE and conductivity the compound containing 50 phr conductive carbon black.

Physical properties

Because of low SE of the rubber composites containing only aluminum powder, these samples were not investigated physical properties. Tensile properties of the black-filled and binary-filler filled rubber composites are shown in Figures 5 and 6 respectively. Figure 5(a) shows that this conductive carbon black decreased tensile strength of NR more than ENR and CSM. The 30 phr of carbon black increased the
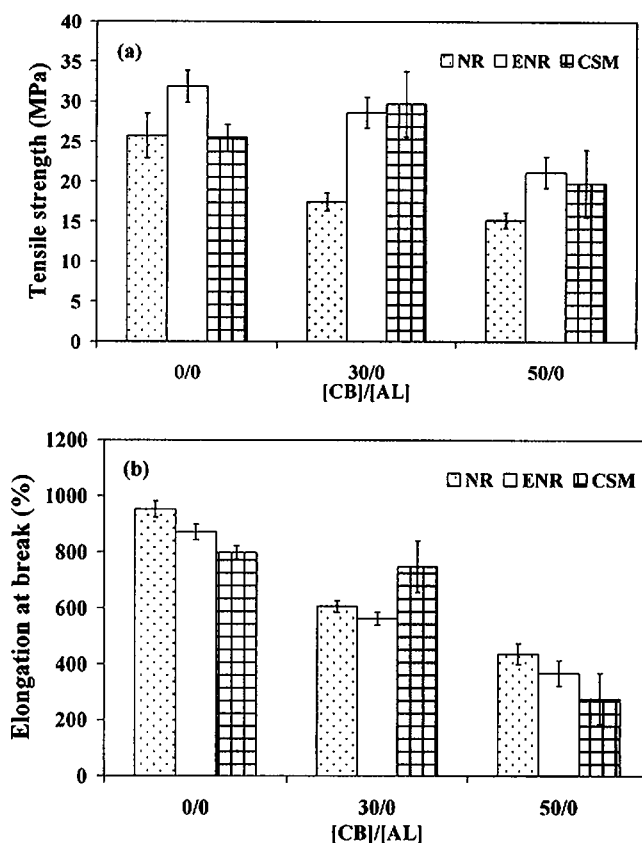

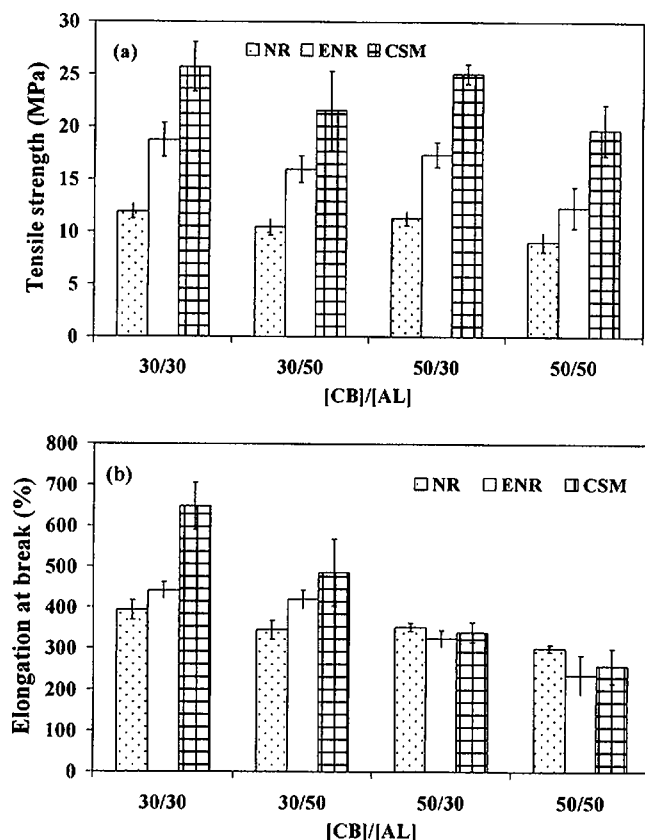**Figure 5** Tensile properties of rubber composites containing carbon black 0, 30, and 50 phr: (a) σ_b; (b) ε_b.

Figure 6 Tensile properties of binary-filler filled rubber composites: (a) σ_b; (b) ε_b.

strength of CSM by approximately 17%, whereas the strength of ENR and NR decreased by about 10 and 32% respectively. Increasing the carbon black further (50 phr) will decrease strength of all rubbers. Similarly to general rubber composites, the higher the filler content the lower the tensile strength, and rubber composites exhibit their own optimal composition. Most deterioration was derived from NR composite, whereby its tensile strength decreased by approximate 41%. Elongation at break of all rubber composites decreased with increasing in conductive carbon black content as shown in Figure 5(b). The degree of reinforcement achieved by incorporation of filler was due to good adhesion between filler particles and matrix. Perhaps the mixing condition was not optimal, therefore tensile strength of the rubber compounds decreased unexpectedly. A decrease in tensile strength of NR black-filled composite should be due to nonpolarity of NR and high polarity of the conductive carbon black. The latter is attributed to the positive impact on tensile strength of CSM and lesser decrease in tensile strength of ENR after applying the appropriate content (the 30/0 sample) into those polar rubbers. The other two factors that should be of concerned are the compatibility between conductive carbon black and ENR/CSM and polarity of these two rubbers. To differentiate compatibility and polarity of ENR and CSM are beyond the scope of this work.

It is well known that Cu, Fe, Mg, and Mn affect vulcanization. Therefore, this study employed Al powder, not Cu powder, although Cu provides higher conductivity than Al. Based on MDR results, Al powder had no effect on vulcanization. Reduction in tensile strength of the binary-filler system as shown in Figure 6(a) was most dominant in NR and ENR composites, and less change was obtained from CSM composites. Tensile strength of the rubber decreased by 64%, 61%, and 22% after adding 50 phr of carbon black and 50 phr of aluminum powder in NR, ENR, and CSM respectively. The binary-filler filled CSM composites maintained high tensile strength ($\geq$20 MPa) for all composition, whereas the tensile strength of those ENR and NR composites were in the range of 10–12 MPa and 13–18 MPa, respectively. Elongation at break of all rubber composites decreased as filler content increased as shown in Figure 6(b). All the 50/50 samples showed low elongation at break (<300%).

Tear strength of rubber composites are shown in Figure 7. In contrast to tensile strength, carbon black and aluminum powder increased tear strength of rubbers, and the most increase was obtained by CSM
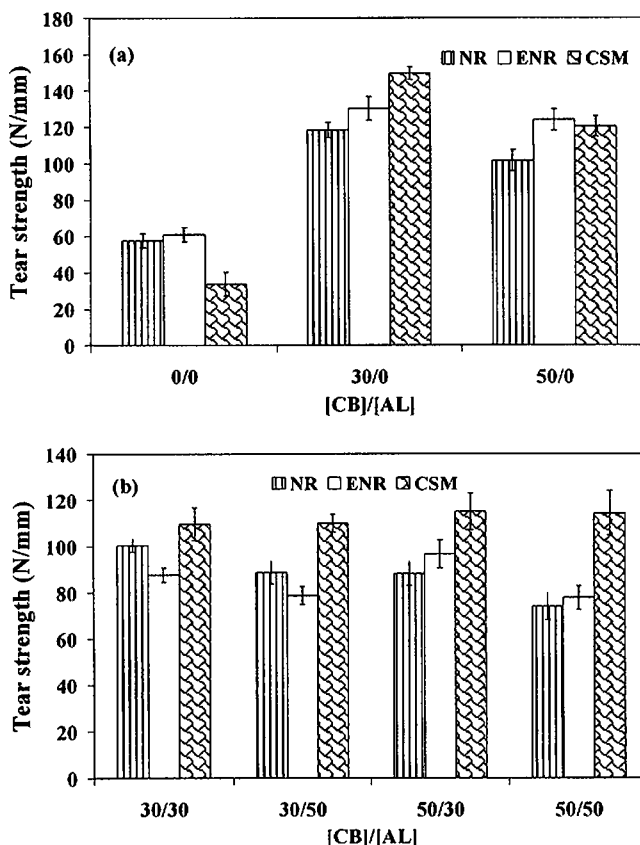

Figure 7 Tear strength of rubber composites: (a) single filler-filled rubber composites; (b) binary filler-filled rubber composites.

TABLE V
Hardness of 12-mm-thick Rubber Composites (Shore A)

[CB]/[AL][a]	NR	ENR	CSM
0/0	38	45	45
30/0	56	71	80
50/0	68	80	94
0/30	50	63	61
0/50	63	66	68
30/30	67	78	87
30/50	73	80	91
50/30	77	88	96
50/50	81	89	97

[a] Ratio in phr, [CB] = carbon black, [AL] = aluminum powder.

TABLE VII
Compression Set (%) of 12-mm-thick Rubber Composites at 27°C and 70°C for 22 h

[CB]/[Al][a]	NR		ENR		CSM	
	27°C	70°C	27°C	70°C	27°C	70°C
0/0	2.19	25.08	44.12	76.04	37.14	71.70
30/0	17.12	47.51	27.35	53.27	18.64	36.23
50/0	25.49	54.88	31.95	73.04	23.55	40.42
0/30	8.23	24.04	17.38	59.14	28.62	73.06
0/50	10.50	32.92	24.61	57.05	25.62	49.42
30/30	10.79	25.70	39.03	53.00	26.11	58.37
30/50	14.48	35.22	48.71	62.80	33.51	70.12
50/30	22.36	58.72	44.13	53.84	24.57	71.46
50/50	24.74	68.59	52.84	70.02	22.74	71.92

[a] Ratio in phr, [CB]: carbon black, [AL]: aluminum powder.

composites. The composites containing 30 phr of carbon black seems to be the best composition in terms of mechanical properties. Addition of the aluminum powder in the black-filled composites will lower the tear strength, except the CSM composite. The increase in tear strength of rubber composites synchronized with the increase in hardness represented in Table V. Both fillers increased the hardness of rubber, and carbon black showed stronger effect resulted from more volume fraction. More filler loading yielded higher hardness. NR composites were softest and CSM composites were hardest.

Thermal aging resistance was reported in terms of changes in tensile properties and tabulated in Table VI. The positive values indicate the appearance of crosslinking during aging, and negative values indicate molecular scission. Crosslinking in CSM and scission in NR along thermal oxidation are well established. Therefore, the negative change in tensile strength was observed in NR and ENR, whereas the increase in tensile strength was observed in CSM. Binary-filler caused more changes than carbon black. All the 50/50 samples showed large changes in tensile strength and elongation at break, except elongation at break of CSM.

Compression set is another important property of rubber for certain applications such as gasket. Low compression set is required in such application. All three rubber composites showed relatively high compression set at high temperature as listed in Table VII. At ambient temperature NR without fillers had very low compression set whereas ENR and CSM had higher values. Both fillers increased compression set of rubber and carbon black showed stronger effect which may be due to its applied higher mass. Although the binary-filler filled ENR and CSM composites, particularly the 50/50 samples, showed high SE and high tensile properties and tear strength, their compression set at high temperature is not acceptable.

CONCLUSIONS

Microwave absorbing rubber composites was prepared by adding conductive carbon black and aluminum powder in NR, ENR, and CSM. SE of each sample was in the same range under the entire frequencies (8.5–12 GHz) and the effect of fillers on SE of three rubber systems was similar. SE of the rubber increased from < 1 dB to 18–28 dB after adding 50 phr of carbon black or to 30–40 dB after adding 50 phr of carbon black and 50 phr of aluminum powder. Although the conductivity was higher, aluminum powder was less effective than conductive carbon black because of the lower volume fraction and larger grain size. Binary-filler showed higher SE than single-filler. SE of the rubber composites can be ranked in the following order: ENR ≥ CSM > NR, and a rank of their mechanical properties, except compression set, was CSM > ENR > NR.

TABLE VI
Changes in Tensile Properties (%) of Rubber Composites after Thermal Aging

[CB]/[AL][a]	NR		ENR		CSM	
	σ_b	ε_b	σ_b	ε_b	σ_b	ε_b
0/0	+16	−26	−23	−6	+25	−23
30/0	−14	−33	−16	−20	+16	−1
50/0	−17	−32	−1	−26	+38	−27
30/30	−34	−46	−27	−29	−3	−16
30/50	−36	−51	−37	−42	+10	−6
50/30	−40	−55	−9	−41	−10	−13
50/50	−30	−55	−14	−45	+39	+12

[a] Ratio in phr, [CB]: carbon black, [AL]: aluminum powder.

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