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Electromagnetic interference shielding properties of butyl rubber-single walled carbon nanotube composites

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ABSTRACT

Butyl rubber (BR)-single walled carbon nanotube (SWCNT) (BR-SWCNT) composites were prepared by solution mixing process to evaluate its electromagnetic interference (EMI) shielding efficiency in the X and Ku band (8.2–18 GHz) frequency range for flexible electrostatic discharge shielding applications. Shielding properties of BR improved with SWCNT addition and EMI shielding effectiveness of about 9–13 dB was obtained for the composite with 8 phr of SWCNT loading in the measured frequency range. The experimental results reveal that absorption was the dominating shielding mechanism. The dielectric properties, conductivity and skin depth of BR-SWCNT composite were found to increase with SWCNT loading and were observed to be significant factors influencing EMI shielding properties of the developed composite.

1. Introduction

Electromagnetic interference (EMI) shielding materials have attained great attention in the recent years in modern electronic era due to the mutual interference among the electronic systems which leads to disturbance, false operation of appliances and leakage of information [1,2]. Shielding of electromagnetic radiation in the microwave region especially in the high frequency region of 8.2–18 GHz (X and Ku band) has high importance in the number of fields in today's civilian and military technology [3,4]. Now a days electrostatic discharge (ESD) shielding applications has acquired great attention to protect sensitive electronic components including integrated circuits (ICs), multi chip modules from electrostatic discharge [5]. Modern electronic industry incorporates measures to prevent ESD events throughout the manufacturing, testing, shipping and handling processes. ESD provides a path to discharge the excess of stored electric charge on an electrically insulated object to an object at a different electrical potential. Static dissipative materials have electrical resistance between insulating and conducting materials [6–8]. Hence, continued efforts have been made to obtain environmentally benign light weight shielding materials with good shielding efficiency, easy processability, preferred physical and mechanical properties.

Polymer composites based on nano sized fillers have unique combination of electrical, thermal, dielectric and mechanical properties. They represent a class of materials for the suppression of this electromagnetic pollution [9–12]. Electrically conductive elastomers can be an exciting solution for environmental and electromagnetic interference, electrostatic discharge and radio frequency shielding by providing a component that can give both environmental and electric sealing. The incorporation of elastomers with conductive materials creates a multi material compound capable of providing electrical shielding with superior flexible and stretchable physical properties of elastomers. Stretchability provides an additional benefit that they can be used in applications to cover curved surfaces, movable parts, can accommodate wide variety of shapes of circuit boards and other components. Hence elastomers combined with a large array of conductive fillers has been utilized for shielding applications in the field of flexible electronics as well as in the aerospace, semiconductor and medical industries. Proper selection of the conductive filler is critical to get the desired electrical and physical properties [13]. Among the elastomers, butyl rubber (BR) is chosen as the matrix because of its good oxidation, ozone and chemical resistance, good mechanical flexibility and biocompatible nature [14]. Typical materials for ESD shielding in the semiconductor and medical industries include carbon-filled silicone and polyurethane blends to shield highly sensitive electronic circuitry [13,15].

Carbon based polymer composites were found to be scientifically attractive materials due to their light weight, good electrical and mechanical properties [16]. Carbon nanotubes (CNT) have attained considerable interest as shielding materials because of its unique physical, electrical and chemical properties. CNTs are

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known for their high strength and toughness, good electrical and thermal conductivity, high aspect ratio and low density etc. CNT-polymer composites offer advantages over other carbon based composites for ESD applications owing to low filler loading level and hence have minimal impact on the physical properties of polymers. Thus CNT based composites have gained momentum due to its use in commercial, military and biological applications [17–20]. EMI shielding efficiency of CNT composites depends on the fabrication techniques, type of CNT, level of filler loading, dispersion of CNTs and nature of host matrix [21].

In the present study, BR-SWCNT composites were prepared by solution mixing process and an attempt has been made to investigate the potential of BR-SWCNT composite as electrostatic discharge shielding material. The effect of SWCNTs on the dielectric properties, skin depth, conductivity and EMI shielding behaviour of BR in the X and Ku band frequency range (8.2–18 GHz) is investigated for the first time to the best of our knowledge.

2. Experimental

The BR-SWCNT composites were prepared by solution mixing method by dissolving 2 wt% of BR in toluene, then adding the activators (zinc oxide & stearic acid), accelerator (tetramethyl thiuramdisulfide) and vulcanising agent (sulfur) into it and were ultrasonicated for 30 min. Single walled carbon nanotubes (SWCNT (Aldrich, Chemical Company, Inc., Milwaukee, WI, USA)) were ultrasonicated for 30 min in toluene and added into the above mixture. The resultant mixture is again ultrasonicated for 60 min and kept to dry in vacuum oven at 60 °C for 12 h [22]. To quantify the ingredients in rubber based compounds, the accepted practice is parts per hundred parts rubber (phr). The SWCNTs were added from 1 to 8 phr into the rubber matrix and compositions of the composites prepared are given in Table 1 [14].

The dried mixture thus obtained were hot pressed at 200 °C under a pressure of 2 MPa for 90 min into rectangular samples of thickness 1 mm for microwave measurements by the waveguide method. The dimension of samples for X band (8.2–12.4 GHz) is 22.86 × 10.80 mm and that for Ku band (12.4–18 GHz) is 15.80 × 7.90 mm. The magnitude of complex scattering parameters S11 and S21 were measured using vector network analyzer (Agilent Technologies E5071C, ENA series, 300 kHz–20 GHz, CA) and EMI shielding effectiveness were calculated. The complex permittivity was determined from the measured scattering parameters with an accuracy of about 2% using Agilent software module 85071E. The DC conductivity of the samples was measured using four probe method from the current and voltage relationships using current source Aplab 9710 P and nanovoltmeter Keithley 2182 A using the same samples used for microwave measurements. Tensile measurements of the BR-SWCNT composites were carried out in a Universal Testing Machine (Hounsfield, H5KS UTM, Redhill, U.K.) with a rate of grip separation of 500 mm/min using dumb-bell-shaped samples of width 4 mm and thickness in the range 1.5–2 mm. The images of the composite were recorded with digital camera (Sony, 10x optical zoom, 16 M pixel). The microstructure of the SWCNT were analyzed by High Resolution Transmission Electron Microscope (HRTEM) (FEI Tecnai-G2 30S-TWIN, FEI Company, Hillsboro, OR) and that of composites using Scanning Electron Microscope (SEM) (JEOL, JSM-5600LV, Tokyo, Japan).

3. Results and discussion

The shielding effectiveness of carbon nanotube filled polymer composites depends on factors such as fabrication technique, type of CNT as well as its level of dispersion in the polymer matrix. Fig. 1(a) and (b) depicts the TEM images of the SWCNT and it can be observed that diameter of individual carbon nanotubes are found to be less than 25 nm and approximately few micrometers in length. The larger diameter of SWCNT is may be due to the agglomeration of SWCNTs as the SWCNT were not functionalized. The SEM images of the fractogram of the BR-8SWCNT composite are shown in Fig. 1(c) and (d). SWCNTs are homogeneously distributed in the BR matrix, even though some agglomerations are found. This composite has SWCNT loading of about 3.5 vol% in the BR matrix along with other additives. Due to the low filler loading, the carbon nanotubes in the composite are covered with butyl rubber and hence are invisible in the SEM images. Photographic images of BR-8SWCNT composite are given in Fig. 1(e) and (f). The flexibility of the composite is clear from the photograph of folded BR-8SWCNT composite shown in Fig. 1(f). The flexibility of the BR-SWCNT composite is more evident from the stress–strain curves shown in Fig. 2. It is found that even at 1000% of strain, the higher filler loaded composite (BR-8SWCNT) doesn't break indicating that the composites are flexible enough to meet the requirements.

The variation of relative permittivity (ε_r) and dielectric loss tangent ($\tan\delta$) of BR-SWCNT composites with increase in SWCNT loading at the mid frequencies of X and Ku band (10 & 15 GHz) are shown in Table 2. The relative permittivity is found to increase with SWCNT loading at both 10 and 15 GHz of frequencies. The relative permittivity increases from 2.4 to 14 as the SWCNTs loading increases from 0 to 8 phr at 10 GHz and increases from 2.3 to 13 at 15 GHz for the same increase in filler loading. Dielectric relaxation and motion of conducting electrons are mainly responsible for the relative permittivity [23]. The SWCNTs have free charge carriers and thus contribute to the increase in relative permittivity of BR-SWCNT composite with SWCNT loading due to the interfacial and electronic polarization mechanisms [17,23,24]. The dielectric loss tangent of BR-SWCNT composite also increases almost ten times with increase in SWCNT loading from 0 to 8 phr at the two frequencies. The conductivity of SWCNTs is higher due to the presence of charge carriers which leads to higher imaginary part of permittivity and thus results in the increase of dielectric loss tangent with increase in SWCNT loading.

Conductivity of a material considerably influences its EMI shielding property. Fig. 3(a) depicts the variation of AC conductivity of BR-SWCNT composite in the frequency range of 8.2–18 GHz with SWCNT loading. The AC conductivity is given by $2\pi f\varepsilon_0\varepsilon''$, where f is the frequency, ε_0 is the relative permittivity of the free

Table 1
Formulations of composites used.

Composites	Butyl rubber	Zinc oxide	Stearic acid	Tetramethyl thiuramdisulfide	Sulfur	SWCNT
Parts per hundred rubber (phr)						
BR	100	5	3	1	0.5	0
BR-1SWCNT	100	5	3	1	0.5	1
BR-2SWCNT	100	5	3	1	0.5	2
BR-4SWCNT	100	5	3	1	0.5	4
BR-6SWCNT	100	5	3	1	0.5	6
BR-8SWCNT	100	5	3	1	0.5	8