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Screen printed silver patterns on $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ - Epoxy composite as a strategy for many-fold increase in EMI shielding

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ABSTRACT

The thermal, mechanical and dielectric properties of epoxy resin were improved substantially after making it a composite with the perovskite oxide conductors $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSCO). Nevertheless, the electromagnetic interference (EMI) shielding characteristics of the composites (in the X and Ku-band) were not up to the level for practical applications which prompted us to introduce a novel strategy to augment the level of shielding. On top surface of the composite sheets, predesigned silver (Ag) patterns (periodic structures like rectangular patterns parallel and perpendicular to the waveguide axis, mesh like patterns as well as blanket coating) were screen printed, which resulted in a dramatic 4-fold improvement in their EMI shielding effectiveness, with significant enhancements in the reflection and absorption shielding efficiency of the composite. Compared to the conventional way of adding silver to form epoxy-silver 0–3 composite above its percolation, the present method of screen printing needs only lesser amount of the conductor to generate a maximum shielding efficiency of 99%, with considerable easiness of processing.

1. Introduction

In a rapidly advancing world, the term pollution is inevitable which affects every walk of life. While looking at electronic pollution, a recently highlighted domain that has far reaching consequences is electromagnetic pollution which is an obvious outcome of the fast growing digital and telecommunication sectors. Electromagnetic interference (EMI) is a major threat to the electronic world [1,2] that may degrade the performance of the circuit or even stop it from functioning [3]. There arises the need for the electromagnetically compatible (EMC) systems which are concerned with the design and operation of an electrical and electronic system. EMC can be achieved by using an EMI shielding material at the emitter or susceptor.

While searching for EMI shielding materials, a variety of materials can be suitable with wide range of properties like electrical conductivity, magnetic permeability and geometries. Shielding can be either absorptive or reflective [4,5]. Metal based shielding materials are good in reflective shielding [6]. The easy way to incorporate a shielding structure, say a metal, to a component is through the route of polymer composites. However, most of the polymers are insulators and are transparent to electromagnetic radiation [7]. To metalize the polymers, there are several techniques available. Some of the available techniques includes making composites of polymer with metallic particles [8,9,10], making conductive coatings through various printing techniques [11], direct metallization through vacuum metalizing, electro and electroless plating [12,13,14], or establishment of intrinsically conductive polymers [15,16,17]. Among all, the composite approach and conductive coating through printing are seems to be cheaper than other techniques of metallization. Conductive filler incorporated composite is widely used in EMI shielding purpose and the metals used were silver, copper, aluminium, nickel, iron etc. Now the metals are replaced with conducting carbon based materials such as carbon black, carbon nanotube, graphene etc. which are advantageous in a way as they are light weight and non-corrosive, compared to the metals. Thus it became evident that developing novel percolative composites has been a widely adopted strategy to achieve EMI shielding, and relatively less attention has been given to the surface modification of the composites.

Over the years, a few groups adopted screen printing of conducting pastes, especially carbon based pastes, as a means to improve their microwave absorbance on a variety of polymer surfaces [18,19,20]. EMI shielding filters made of Ag-conductive patterns printed on plasma display panels have recently been demonstrated in a few patents as well [21,22]. Designing and printing Ag-based metamaterial patterns on polymer substrates is another popular strategy to suppress certain selective frequency bands detrimental to the operating bands of specific devices [23]. Such structures are termed as frequency selective surfaces

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that can be easily applied as wallpaper on the walls of rooms without any structural loading issues to existing architecture. In another interesting work, silver oxide mesh patterns were bar-coated on a PET film with a thickness of 30 μm [24]. However, this method requires a curing at 150 °C and the synthesis procedure of silver neoalkanoates involves complex procedures. A few isolated studies have also been attempted to print metallic patterns on polymer, as a means to enhance the shielding effectiveness [25,26]. In the present work, $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ - epoxy composites were employed as the platform for building up novel EMI shielding structures. In order to make a dramatic improvement in its EMI shielding characteristics, a unique approach of printing patterns of conductive Ag on top of the composite surface, was adopted. The microstructure, electrical and microwave dielectric properties of the various printed EMI shielding structures were investigated in this manuscript.

2. Experimental

LSCO powders were prepared by conventional solid-state reaction route. The constituent chemicals La_2O_3, $SrCO_3$, and Co_2O_3, (Aldrich, 99%) were weighed stoichiometrically and mixed thoroughly in distilled water through ball milling using zirconia balls as the milling media, for 24 h. The uniform slurry, dried in a hot air oven at 100 °C was calcined at 1100 °C for 4 h to get the phase pure LSCO. The composite was prepared by mechanically mixing LSCO powder with the room temperature curable epoxy resin (Huntsman resins; Araldite® GY 260) for 30 min in a steel vessel. Before proceeding to the next step of addition of curing agent, there involved a degassing procedure to eliminate the entrapped gas in the LSCO-epoxy matrix. Further step involved the addition of amine-based curing agent (Aradur® 1012) to the degassed matrix. The ratio of epoxy resin to the curing agent was kept to be in the ratio of 10:2.5 as suggested by the manufacturer. After thoroughly mixing the curing agent with the LSCO-epoxy matrix, it was transferred to appropriate mould and kept at room temperature for 24 h for complete curing. The prepared composite sheets were polished to suitable dimension for shielding effectiveness studies. For coating of the conductive metal patterns, a commercial grade silver ink (Metalon HPS-030LV, Novacentrix, USA) was used. Screen printing of silver ink on the surface of small rectangular composite sheets were carried out using a home-made screen printer (Plastomec, Kerala). The optimal level of Ag line width was adjusted to be ~300 μm and the same width was maintained for the vertical, horizontal lines as well as mesh designs.

2.1. Characterization

The microstructure of the composites was analyzed using a scanning electron microscope (SEM) (Jeol Model, JSM 5600LV). Atomic force microscopy (AFM) imaging was performed under dry conditions at room temperature using MultiMode 8 AFM equipped with NanoScope V controller (Bruker, Santa Barbara, CA, USA). Si cantilevers (NSG 01, NT-MDT) were used with force constants in the range of 2.5–10 N/m and with resonance frequency in the range of 120–180 kHz. The scan rate used was 0.5–1 Hz. Raw data were processed offline using Bruker's NanoScope Analysis image processing software. Surface roughness was reported both in average roughness, root-mean-square (RMS) values. The compressive strength of the composites was measured according to the ASTM standard C365/C365M-05 using a universal testing machine (Instron 5500 - USA). The cylindrical samples of 15 mm diameter and 30 mm height were used for the characterization. The test was carried out at a cross-head speed of 2 mm/min.

The EMI shielding effectiveness (SE) of the screen printed samples was measured in X and Ku band region, using a vector network analyzer (Agilent E5071C) by fixing the surface coated composite sheets in a transmission wave guide. The dimensions of samples were different for measurement in X and Ku bands. For this, we used suitably machined rectangular blocks of dimensions 22.8 mm × 10.1 mm × 2.0 mm and 15.8 mm × 7.9 mm × 2.0 mm for X and Ku bands respectively. Standard calibration steps were followed prior to the measurements, so as to eliminate the errors due to source match, directivity, load match, isolation, etc. The magnitude of complex scattering parameters (S_{11} and S_{21}) of these composites was measured first. From the measured S_{11} and S_{21} parameters, the EMI shielding effectiveness (EMI SE), absorption shielding effectiveness (SE_A) and reflection shielding effectiveness (SE_R) were calculated. The complex permittivity at microwave frequencies was determined using Agilent software 85071E from the measured scattering parameters.

3. Results and discussion

3.1. Improved thermal, mechanical and dielectric property

Very recently, the effect of LSCO addition on the physical properties of the LSCO-epoxy composite has been studied by Dijith et al. [27]. That study revealed that the optimal mechanical and thermal properties of the composite were at 60 wt% of LSCO loading. For example, the thermal conductivity (TC) of pure epoxy was 0.25 W/m·K, which got improved by 2.3 folds with the incorporation of 60 wt% of filler LSCO. On the other hand, a decreasing trend was observed for thermal expansion with filler loading and the least expansion was optimised to be for 60 weight loaded LSCO-epoxy composite [Fig. 1(a)]. The lower coefficient of thermal expansion (CTE) of LSCO and increasing interfacial area were posing restrictions to the heat induced expansion of epoxy chain. The mechanical behavior of pure epoxy and 60 wt% LSCO loaded epoxy composites (60 LSCO), subjected to increasing compressive strains, is plotted in Fig. 1(b). The compressive strength of the composite was found to be improving with addition of LSCO and observed a maximum compressive strength for the composite with 60 wt% loading. Further addition of filler keeps the compressive strength decreasing due to the inevitable filler agglomeration. The inset of Fig. 1(b) shows the compressive strength of bare epoxy and that of 60 LSCO. Evidently, the value of 62 MPa for pure epoxy got improved to 107 MPa with 60 wt% of LSCO filler addition. The strong interfacial interaction between LSCO and epoxy matrix with an effective stress transfer between them contributes to the observed trend [28,29].

The AFM (3D) surface topography images of the polished surface of the 60 LSCO is shown in Fig. 1(c). From the analysis of the AFM image, it is clear that the average and the root mean square (RMS) roughness values of the surface obtained are 144 and 179 nm, respectively.

3.2. Modification using conductive surface designs

Even though various physical properties such as thermal, mechanical and dielectric parameters of epoxy matrix got improved with 60 wt % loading, the improvement in EMI shielding values were feeble and this situation demands for further modification of already developed composite. A simple strategy was implemented, which involved the introduction of conductive coating on the surface of composite. A schematic representation of the different processes involved in the development of Ag coated LSCO-epoxy composite, is briefed in Fig. 2(a). The different schemes of silver patterns printed on top of LSCO-epoxy composite are pictorially represented in Fig. 2(b). Photographic images of sample holder of the waveguide with bare composite and Ag pattern printed composite were given in Fig. 2(c). A commercially available silver ink (Metalon HPS-030LV) was chosen for screen printing. Composite sheets with optimum thickness (2 mm) and solid loading (60 wt % LSCO) have been selected for implementing the patterns, based on the EMI shielding measurements made on specimens with varying thickness (Fig. 1(d)). The line patterns of silver ink on the composite surface can be assumed as vertical and parallel rectangles (see Fig. 2(b)), with respect to their position in the rectangular slot of the wave guide. Mesh patterns, in a way, is a combination of vertical and parallel rectangular lines, one laid over the other, while the final choice