SYNERGISTIC EFFECTS OF DOPED POLYANILINE AND CARBON BLACK FOR LIGHTNING STRIKE PROTECTION OF COMPOSITES

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ABSTRACT

The effect of using conductive fillers on the overall electrical conductivity of epoxy matrix has been analysed in this paper. A micromechanical model has been developed to study the variation of electrical conductivity with varying volume fraction. The fillers were modelled as circles randomly placed in a square matrix. A hard-core soft-shell approach was adopted where the fillers were modelled as three concentric circles. The innermost circle represented the hard-core such that two adjacent inner circles couldn't intersect. The middle layer had the same conductivity as the inner circle. Only difference was that it could intersect any neighbouring circle. Finally, the outermost circle had electrical conductivity which reduced radially according to a given logarithmic relation. The two conductive fillers used were Polyaniline (PANI) and Carbon Black (CB). The variation of conductivity with different filler concentration was analysed for the individual fillers and the percolation threshold for both the fillers was determined. Then, the synergistic effect of the two fillers combined together in epoxy matrix was studied. The percolation threshold for PANI was found to be 15% filler concentration and that for CB was found to be 20% filler concentration. For the combined filler, three cases of different combinations were tried. It was observed that regardless of the combination used, there wasn't much effect on the overall conductivity of the matrix. However, this combination can be used to even out any disadvantage of the individual fillers. This enhanced epoxy can be used as a coating on composites for damage mitigation against lightning strikes. It has to be experimentally tested to establish its validity.

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1 INTRODUCTION

Fibre-reinforced composites have widespread applications in various fields of engineering, like in the aerospace industry, energy sector, automobiles etc. They have numerous advantages over conventional metals, in terms of superior strength-to-weight ratio, superior stiffness-to- weight ratio, corrosion resistance etc. Aircrafts are slowly replacing conventional metals with these composites. This means that aircrafts can be designed to carry similar payloads at reduced net weight. This results in fuel saving and usage of smaller engines, thus reducing the overall environmental impact. The Boeing 787 Dreamliner reported that it uses 50% of composite by weight. Other material contents include 20% Aluminium, 15% Titanium, 10% steel and 5% other materials. [1] This shows that composites form the majority among the materials in these structures.

However, one major disadvantage of these types of materials is that they are susceptible to damage by lightning strike. A lightning strike can be described as a phenomenon in which there is electric discharge between atmosphere and the ground. It is reported that lightning strikes a flight once every 1000 hours of flight time. Lightning strikes are more prevalent between altitudes of 5,000 feet to 15,000 feet. So, airplanes are mostly struck by lightning in clouds especially during the ascent and descent phase of the flight.

Even though there hasn't been any catastrophic damage reported to a flight due to lightning strike, nevertheless the damage that it causes to the aircraft need to be studied extensively. The traditional method used for lightning strike protection is by using metallic meshes (Aluminium, Copper, etc.) over the composite structure. [2] The issue with this method is that it adds to the overall weight of the structure. Moreover, it is not 100% effective due to the presence of holes in the mesh. An alternative is to use conductive fillers like Carbon nanotubes (CNTs) [3], carbon black (CB) [4], conductive polymers like Polyaniline (PANI) [5, 6], Polypyrrole (PPy) etc. These conductive fillers will increase the overall conductivity of the matrix. An important parameter while using these conductive fillers is the percolation threshold. [7] It is the filler concentration at which the conductivity of the blend takes a sudden jump from the matrix conductivity. Further addition of fillers after this does not cause much change in the electrical conductivity.

Several researchers have tried blending conductive fillers in an insulating matrix to enhance the electrical conductivity of the matrix. In this paper, an attempt was made to combine two types of fillers (PANI and CB) and check their overall impact on the conductivity of the modified matrix. A micromechanical model is developed here to check the variation of electrical conductivity with varying volume fraction.

2 METHODOLOGY

A micromechanical model is designed to predict the variation of electrical conductivity with varying volume fraction. The composite is represented using a 2-D Representative Volume Element (RVE). The filler particles are modelled as circles in a square matrix. A hard-core, soft-shell model is adopted to replicate the conductive filler particle behaviour in the matrix. [8] The fillers are modelled as three concentric circles. The innermost circle represents the hard-core conductive filler (PANI or CB). The middle and the outermost circle represent the hopping distance of the conductive filler. The electrical conductivity in the middle layer remains same as the core conductivity. It is assumed that the conductivity decreases radially in the outermost circle according to the relation given below:

$$\sigma_{R_1 R_2}(r_2) = \sigma_2 - \sigma_1 \log r_2 \,, \quad R_1 < r_2 < R_2 \,, \quad r_2 = 0.1\, r_1 \tag{1}$$

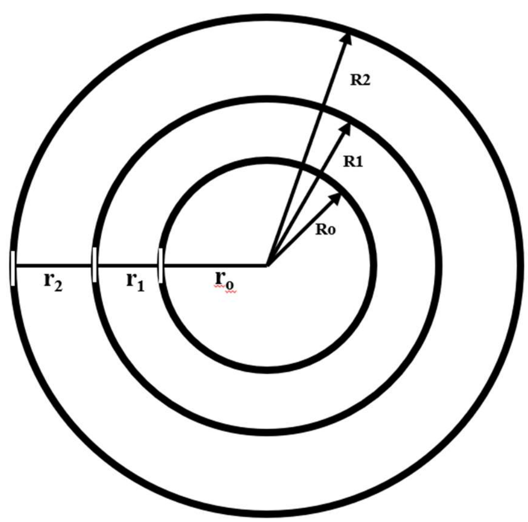

Figure 1: A schematic of the hard-core soft-shell model

The filler diameters for the model were determined from Scanning Electron Microscopy (SEM) images as shown in Fig 2 below. The PANI (doped with Dodecylbenzenesulphonic Acid) particles formed chunks and were not easily distinguishable from the images. So, the PANI diameter was taken from literature as 50 nm. The CB diameter was taken to be 63 nm from the SEM images.

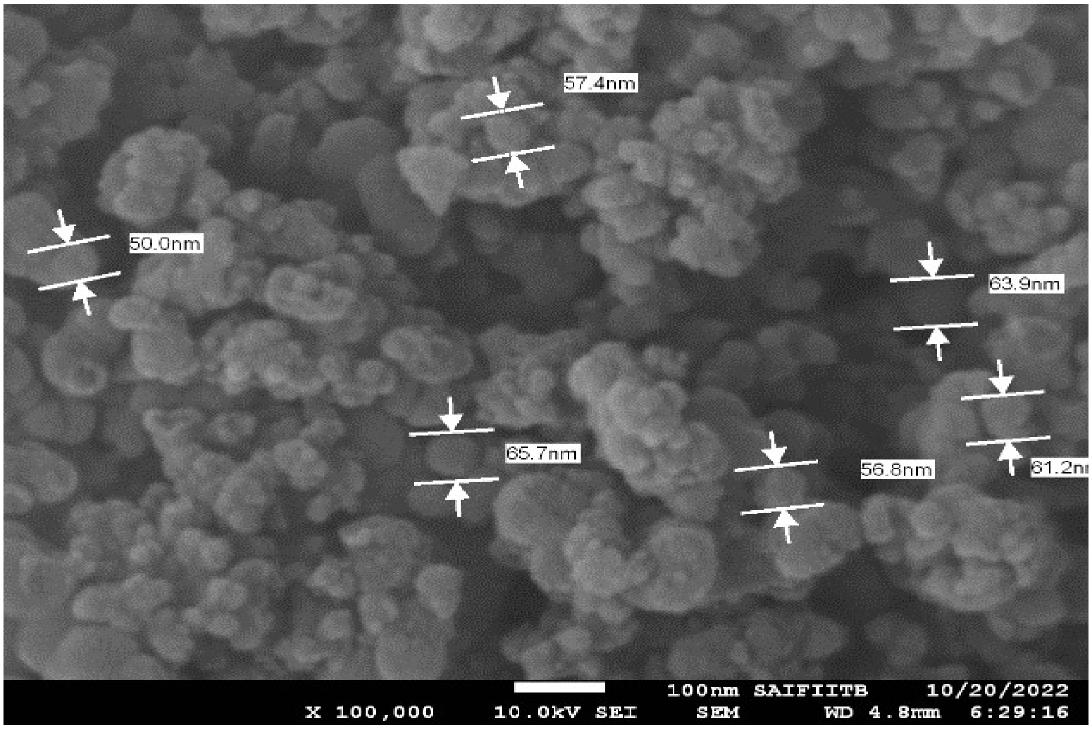

Figure 2: SEM image of Carbon Black

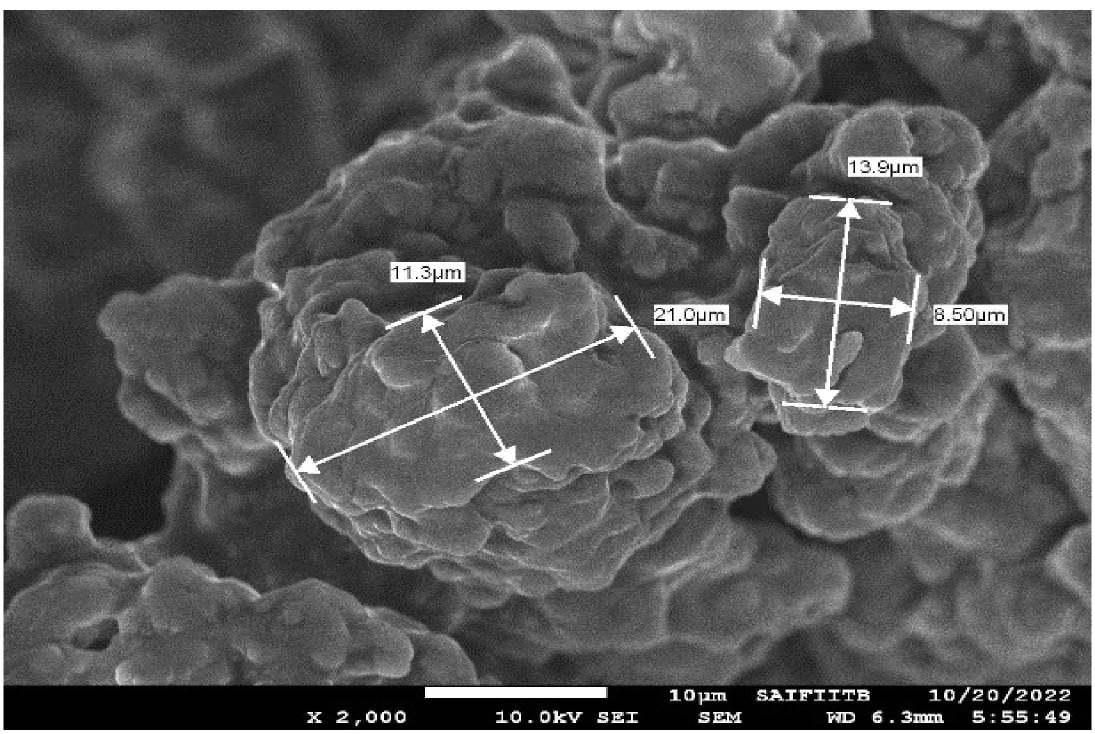

Figure 3: SEM image of Polyaniline

Volume fractions ranging from 2.5% to 30% of the inclusions were studied. An RVE size of 0.005 x 0.005 mm^2 was used. A coupled thermal-electrical solver in steady state was used with a time period of 120 seconds. Only electrical properties of the individual components are applied which will automatically exclude any thermal effects and will only give the uncoupled electrical properties in the output. Two reference points were placed at two opposite faces of the square and an equation type of constraint was used to connect the reference points to their corresponding faces. Degree of freedom (DOF) of 9 was chosen for the equation, which is the DOF for electrical analysis. A potential difference of 1 KV was applied between the two opposite faces through the reference points. A 6-node quadratic triangular coupled thermal-electrical element (DC2D6E) was chosen.

To measure the electrical conductivity, we apply the equation for the electric conduction law given as: [9]

$$J_i = \sigma_{ij} \nabla V_j \quad , (\mathrm{i, j} = 1,2,3) \tag{2}$$

where J_i, σ_{ij} and ∇V_j denote the i-th electric flow rate, the electrical conductivity tensor and the voltage gradient in the j-th direction, respectively. The effective electrical flow rate in the i-th direction is volume-averaged by dividing summation of the element wise contribution to the electrical flow by the volume of the entire RVE as shown in eq below:

$$< J_i > = \frac{1}{\Omega} \int_{\Omega} J_i d\Omega \; = \sum_{k=1}^{nelem} \frac{J_{ik}^{elem} \; d\Omega_k^{elem}}{\Omega} \tag{3}$$

where, Ω, J_{ik}^{elem}, $d\Omega_k^{elem}$ denote the total volume of RVE, the i-th electrical flow rate, and the volume of the k-th element, respectively. Subsequently, $< J_i >$ is divided by the j-th voltage difference ΔVj. Finally, the electrical conductivity tensor (σ_{ij}) is obtained as:

$$\sigma_{ij} = -\frac{< J_i >}{\Delta V_j} \tag{4}$$

Three different cases were studied by varying the filler type: firstly, pure PANI in epoxy was studied by varying the volume fraction from 2.5% to 30%. Secondly, pure CB in epoxy was studied by varying the volume fraction from 2.5% to 30%. Finally, by keeping the filler volume fraction fixed at 20%, three different sub-cases were studied with different combinations of PANI and CB fillers.

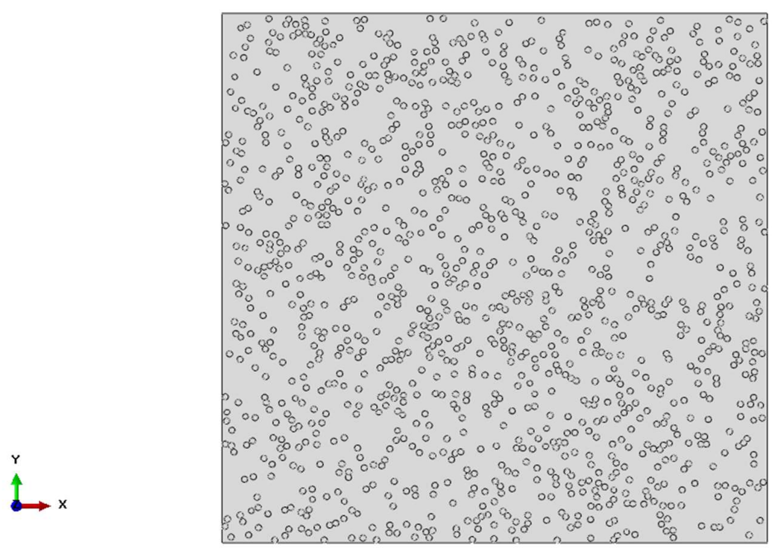

Figure 4: Random filler distribution of PANI at 10% filler concentration

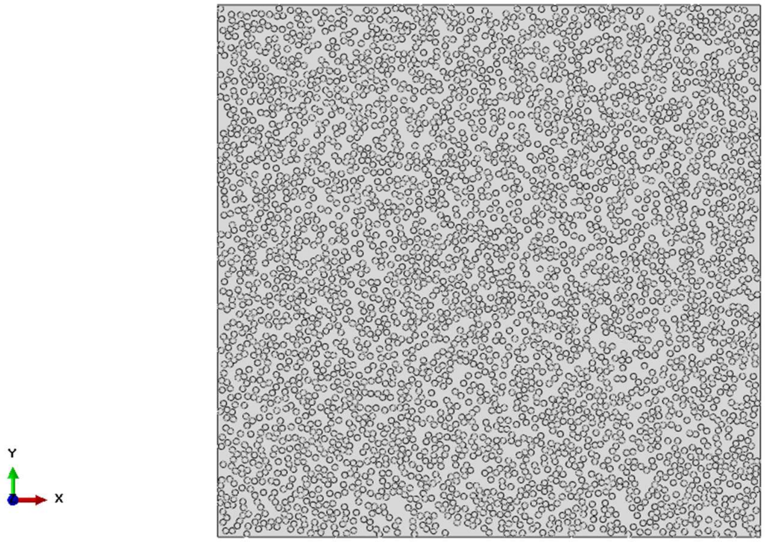

Figure 5: Random filler distribution of PANI at 30% filler concentration

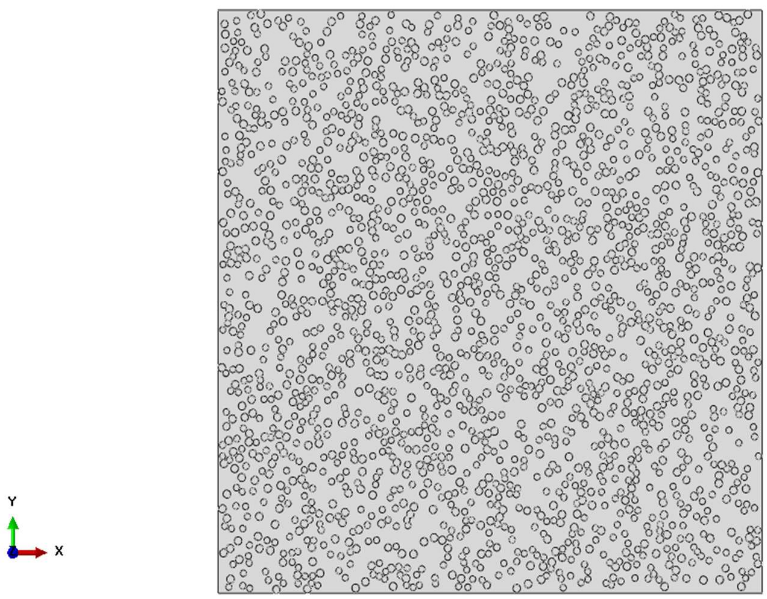

Figure 6: Random filler distribution of PANI and CB combined at 10% -10% filler concentration

The epoxy and filler properties are listed in Table 1 below. [8, 10]

Component	Electrical conductivity (S/m)	Hopping distance (nm)	Diameter (nm)
PANI	1800	2.04	50
CB	5000	2.04	63
Epoxy	7.9e-14	-	-

Table 1: Epoxy and filler properties

3 RESULTS AND DISCUSSIONS

Three different cases were studied as already mentioned above. For the combined filler study, the volume fraction was fixed at 20%. The three different filler combinations used are as follows: 10P10C (10% PANI and 10% CB), 5P15C (5% PANI and 15% CB) and 15P5C (15% PANI and 5% CB).

3.1 PANI/epoxy composite

Volume fractions ranging from 2.5% to 30% of PANI fillers in epoxy were studied in ABAQUS. The variation of the electrical conductivity with varying volume fraction is shown in Fig 7 below. It is observed that the electrical conductivity gradually increases as the volume fraction of the filler increases from 2.5% to 12.5%. After that, we see a sudden jump in the conductivity at 15% filler volume fraction. This suggests that the percolation threshold for the PANI particles in epoxy matrix lies at around 15% volume fraction. After 15% filler volume fraction, the conductivity gradually increases up to 30% volume fraction where we ended our study. Going beyond 30% filler volume fraction is not feasible in reality as the mixture gets too dense. Thus, it becomes difficult to handle and use for different applications.

It is also observed that the error bar increases as the volume fraction of the fillers increase. A possible explanation for this might be that at lower volume fractions, the effect of the filler conductivity on the overall conductivity of the composite is negligible. The matrix conductivity is dominant at lower volume fractions. As the volume fraction increases, the overall conductivity dependence slowly tilts towards the filler conductivity. Thus, the placement of the particles in the matrix plays an important role in determining the overall conductivity of the composite.

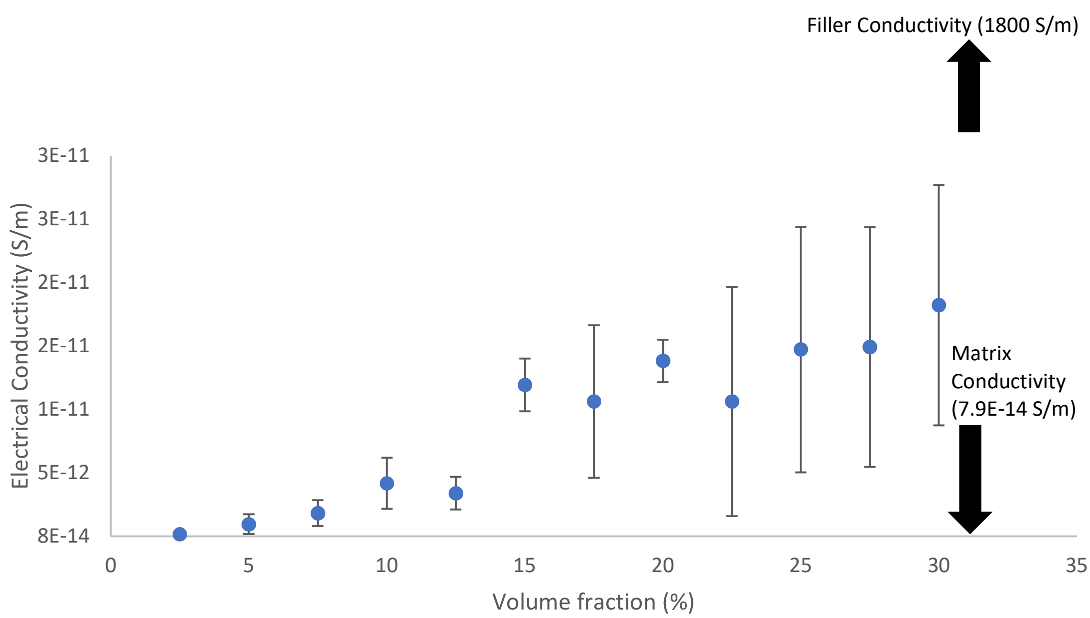

Figure 7: Variation of Electrical conductivity with varying volume fraction in PANI/ epoxy composites

3.2 CB/ epoxy composite

Similar to the PANI/ epoxy composite, CB/ epoxy composite was analysed. Volume fractions ranging from 2.5% to 30% were studied. The variation in the electrical conductivity with varying filler volume fraction was studied. As shown in Fig 8, it was found that the electrical conductivity gradually increases as the filler volume fraction is increased from 2.5% to 10%. After that, at 12.5%, the conductivity takes a jump and it keeps increasing with increasing filler volume fraction. The percolation threshold for the CB filler in epoxy matrix lies around 20% of the filler volume fraction. After that, the electrical conductivity curve forms a plateau even after increasing the filler volume fraction up to 30%.

Similar to the PANI/ epoxy composite, it is also observed in this case that the error bar increases as the volume fraction of the fillers increase. A similar explanation can be provided for the CB/ epoxy composite as well. Similar to the previous case, we have limited our study up to 30% filler volume fraction as it is experimentally not feasible to mix above 30% due to increased density.

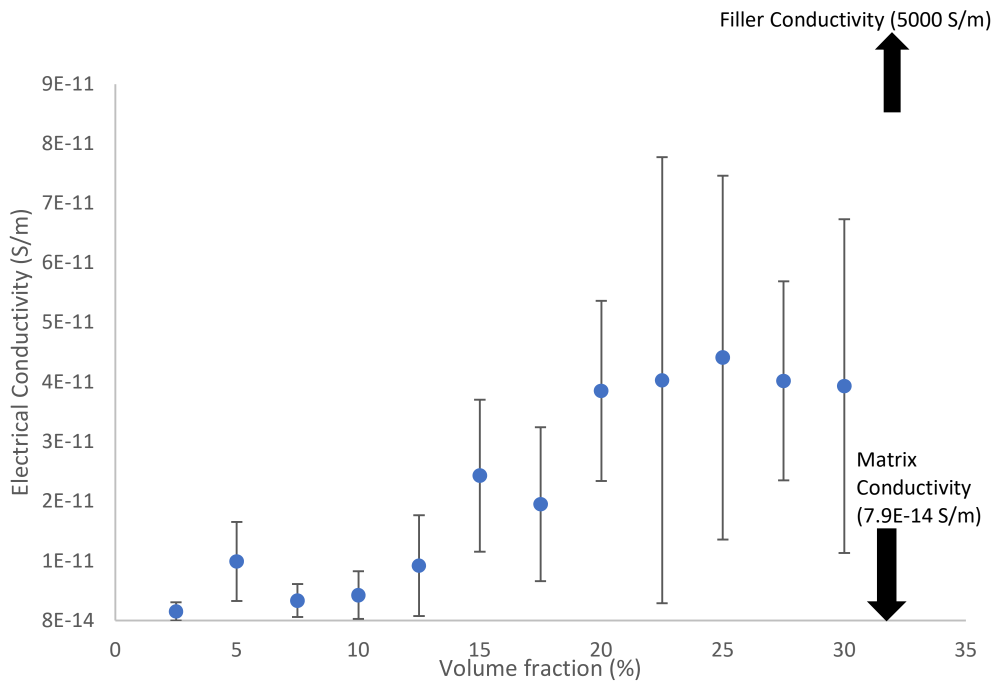

Figure 8: Variation of electrical conductivity with varying volume fraction in CB/ epoxy composites

3.3 PANI-CB/ epoxy

Three different combinations of PANI and CB fillers were mixed in epoxy matrix and their electrical conductivity was checked. The three combinations used were 10P10C (10% PANI and 10% CB), 5P15C (5% PANI and 15% CB) and 15P5C (15% PANI and 5% CB). The variation of the electrical conductivity in all three cases are plotted in Fig9 below. It was observed that there is no significant change in the electrical conductivity in all the three cases. It can thus be said that no matter the combination of filler used, if the total volume fraction remains fixed, there is not much effect on the electrical conductivity of the composite.

It is observed that at similar volume fractions, CB offers higher electrical conductivity than PANI. But the percolation threshold of PANI is found to be lower (around 15%) than that of CB (around 20%). Moreover, the processing of PANI is more complicated than that of CB. PANI in its emeraldine base (EB) form is neutral in nature. It has to be doped with a protonic acid for it to become conductive. In this study, the PANI is assumed to be doped with Dodecylbenzenesulphonic acid (DBSA) which gives the desired electrical conductivity. A compromise has to be made between the two conductive fillers to get the best out of both the fillers.

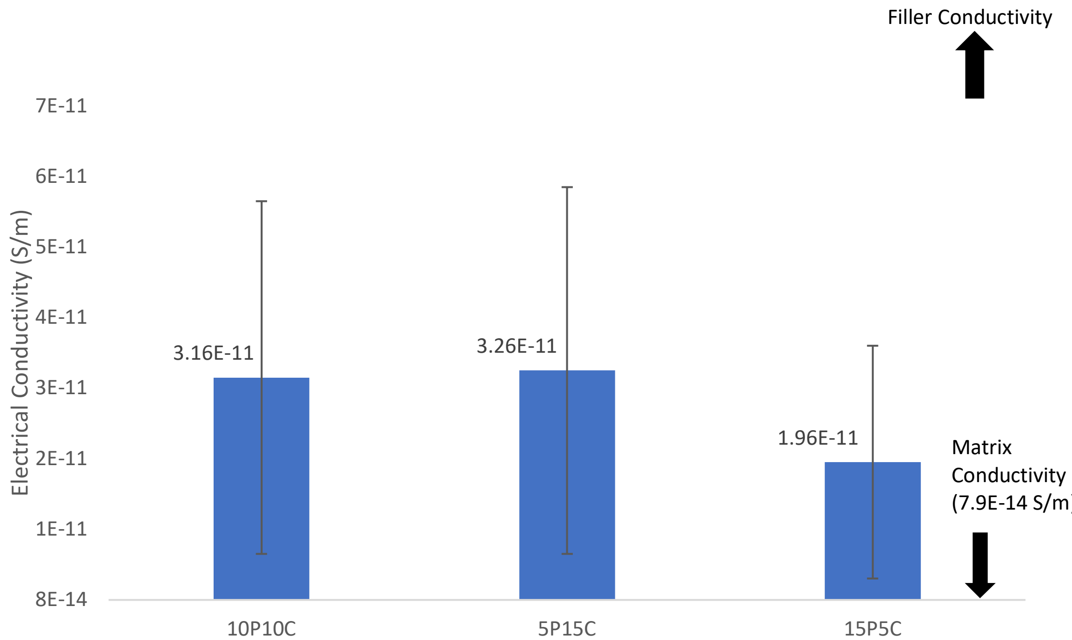

Figure 9: Variation of electrical conductivity for different filler combinations

4 CONCLUSIONS

The insulating nature of fibre reinforced composites is one of the major concern for its application. Researchers are trying to modify this by using different methods. Increasing the conductivity of the matrix using conductive fillers is one of the solutions to this problem. Different types of conductive fillers were studied in the past like carbon nanotubes (CNTs), metallic fillers, carbon black (CB), buckypaper, conducting polymers like Polyaniline (PANI), Polypyrrole (PPy) etc. In this paper, an attempt was made to combine two types of conductive fillers (PANI and CB) to study their combined effect on the overall conductivity of the matrix.

A micromechanical model was developed with random circular inclusions in a square RVE. The particles were generated using a Python script. A hard-core soft-shell model was adopted for the study. Firstly, the variation of conductivity with varying volume fraction of the individual fillers was studied. Volume fractions ranging from 2.5% to 30% were studied for both PANI and CB fillers. It was observed that the percolation threshold for PANI was around 15% while for CB it was around 20% of the filler volume fraction. Then, for the combined filler study, the volume fraction of the filler was fixed at 20% and three different filler combination was tried and their electrical conductivity was analysed. The three combinations were 10P10C (10% PANI and 10% CB), 5P15C (5% PANI and 15% CB) and 15P5C (15% PANI and 5% CB).

It was observed that there wasn't much significant difference in the electrical conductivity in all three combinations. Also, for the same volume fraction, the electrical conductivity in the combined filler is slightly higher than the individual fillers, but the increase in not much significant. This concludes that combining the two filler types (PANI and CB) doesn't have a significant effect on the electrical conductivity of the overall matrix. However, we can still use this combination to negate the disadvantage of the individual fillers. It is also to be noted that the overall conductivity achieved is very less in comparison to metals. So, only using this matrix might not be enough to mitigate the damage due to high current inputs like in the case of lightning strikes. This modified epoxy matrix can be used as a coating on top of fibre reinforced composites to dissipate any incoming high current inputs. The feasibility of this coating as a lightning strike protection system needs to be studied in future.

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