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Non-universal scaling behavior of polymer-metal composites across the percolation threshold

Maheswar Panda [a,b,*], V. Srinivas [a,c], A.K. Thakur [a,d]

[a] *Department of Physics and Meteorology, Indian Institute of Technology Kharagpur, Kharagpur 721302, India*
[b] *Department of Physics, Dr. Hari Singh Gour Central University Sagar, Sagar 470003, India*
[c] *Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India*
[d] *Department of Physics, Indian Institute of Technology Patna, Patna 800013, India*

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ABSTRACT

The universal percolation behavior i.e. $\sigma_{eff}(\omega, f_{con} \approx f_c) \propto \omega^x$ and $\varepsilon_{eff}(\omega, f_{con} \approx f_c) \propto \omega^{-y}$ is satisfied; with $x + y = 1$, where σ_{eff} is the effective ac conductivity of the composite, ω is the frequency of applied ac signal and f_c is percolation threshold. The exponents ($x = 0.72$ and $y = 0.28$) obtained under the inter-cluster polarization model for the case of 3D systems are consistent with the experimental values. The critical exponents s, s' and t which characterize the divergence of ε_{eff} and σ_{eff} in the vicinity of f_c show non-universal values. The non-universality of s, s' and t is correlated with the extent of spatial connectivity of filler particles, which is reflected from the experimental values of loss tangent.

1. Introduction

Polymer-conductor composites (PCC) are attracting much attention because of their physical properties owing to which they often display a significant change if electrically conducting filler's concentration in them is in the vicinity of percolation threshold (f_c). They show a dramatic increase in conductivity and dielectric constant, and therefore could find potential applications, such as; high electric energy density materials, embedded capacitor applications, etc [1–7]. Such PCC are formed by incorporation of different types of conductors, such as; metals [1–9], alloys [10–12], carbon black [13], carbon nano fibers and nano tubes [14–16], graphite nano platelets [17], conducting polymers [18], etc. into the insulating polymer matrix. These composites undergo an insulator to metal transition (IMT) at a critical concentration of the filler material i.e. the f_c at which they show an abnormal increase in dielectric constant and conductivity [19–20]. Among various types of PCC, the polymer-metal composites (PMC) are of particular interest due to their easier processing, cost-effectiveness, high dielectric constant, better flexibility, etc [1–9]. However the f_c value depends on a number of internal parameters, such as; size, shape of the filler, wetting and adhesiveness of the polymer, interfacial interaction and spatial distribution of both the components. In addition to these, processing parameters, such as; temperature, curing time, mixing time and thickness of the composite are also crucial in determining the f_c [8,14,15]. Since a number of parameters affect the f_c value, the experimental observation of an ideal f_c [19,20] is very rare and the percolation behavior of PCC/PMC still requires a clear and better understanding. Therefore it is important that the samples should be prepared under identical conditions for the comparison of properties and to propose any possible physical reason to explain the unusual behavior exhibited in such PCC/PMC. Theoretical calculations on PCC/PMC suggest that at f_c a singularity in effective dielectric constant (ε_{eff}) is expected [19,20]. However experimentally the value of ε_{eff} and its extent of enhancement at f_c for different PMC are found to be different [1–9]. Although PMC give higher dielectric constant as compared to ceramic polymer composites, a further enhancement of dielectric constant is also desirable for various applications. Thus, the study on the origin of large values of ε_{eff} and its extent of enhancement at f_c for PMC is desirable for several applications mentioned in the above discussion. It is predicted that in a random distribution of conducting particles embedded in an insulating matrix [through a three dimensional (3D) random circuit network in which the components are either pure resistances (R) or pure capacitances (C)] the ε_{eff} and effective conductivity (σ_{eff}) follow universal fractional power laws as a function of frequency in the vicinity of f_c [13,21–24], which are given by

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* Corresponding author at: Department of Physics, Dr. Hari Singh Gour Central University Sagar, Sagar 470003, India. . Tel.: +91 7582 265459.

E-mail address: panda.maheswar@gmail.com (M. Panda).

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$$\varepsilon_{eff}(\omega, f_{con} \approx f_c) \propto \omega^{-y} \quad (1)$$

and

$$\sigma_{eff}(\omega, f_{con} \approx f_c) \propto \omega^{x} \quad (2)$$

where f_{con} is the volume fraction of conductor in the composite, ω is the frequency of an applied ac signal, x and y are the critical exponents and they are expected to satisfy the relations $x + y = 1$ [13,19–26], with $x = t/(s + t)$ and $y = s/(s + t)$ under the intercluster polarization i.e. the RC model [13,21–29], where s and t characterize the divergence of ε_{eff} and σ_{eff} in the vicinity of f_c. According to percolation theory [19,20], the power law behavior of ε_{eff} and σ_{eff} in the vicinity of f_c is given by;

$$\varepsilon_{eff} \propto (f_c - f_{con})^{-s} \text{ for } f_{con} < f_c \quad (3)$$

$$\sigma_{eff} \propto (f_c - f_{con})^{-s'} \text{ for } f_{con} < f_c \quad (4)$$

$$\sigma_{eff} \propto (f_c - f_{con})^{t} \text{ for } f_c < f_{con} \quad (5)$$

where 's' is the dielectric exponent in the insulator region and 's', t' are the conductivity exponents in the insulator and conductor region respectively. According to the two different physical models [13,22], such as; the intercluster polarization model (RC model) [13,21–29], and the anomalous diffusion model [30–32], the 3D universal values of critical exponents are $x = 0.72$, $y = 0.28$ and $x = 0.58$, $y = 0.42$ respectively. According to the percolation theory [19,20] in 3D, under the consideration of inter-cluster polarization model, the relations $x = t/(s + t)$ and $y = s/(s + t)$ are valid and the universal values of s, s' and t are given by $s_{un} = s_{un}' = 0.7–1$ and $t = 1.6–2.0$. But in most of the practical continuum percolation systems (PCC) [19,20,22,33–36], the critical exponents are found to be higher than the universal values which has been explained by various un-usual models, such as; the position space renormalization group approximation model [21], the random void model/the swiss cheese model and the inverted swiss cheese model [37–41], etc. Sometimes the exponents deduced are not related to percolation effects, but, more or less, to experimental artifacts [42]. No clear understanding regarding the increment and the extent of deviation of the critical exponents (s, s', t) from their respective universal values (i.e. the quantification of the increment in terms of any experimentally measurable physical parameter) is found in the literature. Hence the quantification of the deviation of scaling exponents from their respective universal values in terms of an experimentally measurable physical parameter which tailors the extent of increment of the critical exponents can give the understanding in a different way.

In this work, it is shown that with lower metal loading in a PMC, a higher ε_{eff} at f_c is observed as compared to earlier reports. In addition to "boundary layer capacitor effect" [1–18] it seems the net work of connectivity for the conducting path and the number of blockages/blocking area for the charged carriers is the crucial factor for enhancement of the ε_{eff}. We also found that although the number of micro capacitors formed in the sample result in higher magnitude of ε_{eff} but it is the series or parallel combination of the micro-capacitors, which plays the major role in providing the enhancement of ε_{eff}. The critical exponents are found to be different from their universal values and their values vary with the extent of connectivity in a PCC in such a way that the universal percolation behavior of $x + y = 1$ is well satisfied.

2. Experimental details

In order to achieve the final objectives, several PMC have been prepared with different processing parameters, such as; different filler particle size, different polymers, different process conditions. In studying the different composites, Table 1 gives the details of various series of samples studied in this work. Subsequently the micro structural, thermal and electrical characterizations have been performed on all these samples and the details of electrical characterizations can be found from earlier literatures [3,4,8,9,11].

Table 1
The details of various series of samples with their process conditions and labeling.

Sample	Label	Process conditions
PVDF/μ-Ni[3]	A	Cold pressed at 10 MPa @ room temperature for 5 min
PVDF/n-Ni[4]	B	Cold pressed at 10 MPa @ room temperature for 5 min
PVDF/μ-Ni	C	Hot molded at 10 MPa @ 200 °C for 45 minutes
PVDF/n-Ni[9]	D	Hot molded at 10 MPa @ 200 °C for 45 min
PVDF/n-QC[11]	E	Cold pressed at 10 MPa @ room temperature for 5 min
LDPE/n-Ni[9]	F	Hot molded at 10 MPa @ 130 °C for 30 min

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the large area surface scan of optical micrographs, wherein one can see the brighter regions are the filler particles/-clusters in the background of the polymer matrix. It can be seen that in case of the percolative cold pressed samples of series B and E the size of nano filler clusters is of same order and they are well isolated from each other. Similarly, in series A samples the homogeneity of the samples is maintained with micron size particles dispersed in polymer matrix. In case of the hot molded samples [series C, D and F] the cluster size of the metal filler particles increases and the extent of in-homogeneity increases due to the diffusion of particles, resulted due to heating. The microstructure of the percolating samples in all cases has been confirmed as the parallel combination of resistor and capacitor networks and its correlation ship with various electrical parameters and different electrical relaxation mechanisms has been well explained in earlier literatures [3,4,8,9,11]. Although the network of connectivity of the metallic clusters in the polymer matrix is confirmed to follow RC-type combination, we observe the extent of connectivity of the metallic filler particles is different in all cases with a difference in the size of the metal filler clusters as well as the homogeneity of the samples. This result is due to the difference in f_{con} and process conditions for the respective composites (Fig. 1).

3.2. Dielectric results as functions of frequency and f_{con}

In order to find the relationship between the extent of enhancement of ε_{eff} at f_c to the connectivity of fillers in PMC, ε_{eff} and change in loss tangent [ΔTan δ] [43] (which is calculated as a measure of connectivity of the filler particles/clusters in a PMC) with respect to the pure polymer as a function of f_{con} for all series are shown in Fig. 2. The ε_{eff} rises with increase of f_{con} and increases abnormally at their respective f_c for different PMC. The f_c found for A, B, C, D, E and F are 0.57, 0.28, 0.25 < f_c < 0.26, 0.07, 0.23, 0.06 respectively. We observe the difference in magnitude and the extent of enhancement of ε_{eff} for all PCC at their respective f_c. Generally the enhancement in ε_{eff} in the neighborhood of f_c is explained on the basis of "boundary layer capacitor effect" [1–18]. Earlier reports showed that higher fraction of metal loading enhances the ε_{eff} due to formation of more interfaces in a composite and thus leading to increase in accumulation of charges at the interfaces and enhancement in ε_{eff}. It was also believed that the number of micro capacitors increases with increasing metal content in the composites which gives rise to high ε_{eff}. But we observe from Fig. 2(a) that even though the f_c value is significantly different for different series of samples under study, the magnitude of ε_{eff} for all the composites